

Binding of two cationic compounds with graphene oxide: comparative analysis and observation of synergetic effect

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The present paper reports on the results of the joint interaction of two organic cationic compounds of different structure and nature, namely bisquaternary ammonium decamethoxinum (Dec) with flexible dication and methylene blue (MB) with heterocyclic planar cation, with graphene oxide (GO) in aqueous dispersion. The qualitative differences in the 3D structures of GO modified in binary (GO+Dec), (GO+MB) and ternary (GO+Dec+MB) systems were observed and described on the basis of the UV-vis spectral analysis of the systems. On mixing the components of the binary (GO+Dec) system, a rather rapid gelation of GO dispersion was observed. The appearance of binary (GO+MB) system showed dependence on GO to MB ratio: at low GO content, MB-induced coagulation of GO to tiny bluish flakes took place followed by their sedimentation with time while at high GO content, the GO complexes with MB preserved solubility in water. The result of the joint addition of both Dec and MB to GO dispersion differed qualitatively from the above results of action of individual components. On creation of the (GO+Dec+MB) ternary system rapid flocculation of all components of the system was observed resulting in the formation of dark residue surfacing over the purified decolorized liquid. UV-vis spectra of the liquid phase showed suppression of the lines of all components or their complexes practically to the baseline. The compression of (GO+Dec+MB) composite to flocs is explained by the matching of the size of MB cation to that of Dec dication linker, which provides tight filling of the gaps between GO sheets. The observed flocculation effect in the (GO+Dec+MB) system may be of practical interest in the development of nanocomposite and sorption materials. Information on the features of GO interactions with organic cations differing in structure may be useful for advances in drug delivery problem.

Keywords: graphene oxide, organic cations, methylene blue, decamethoxinum, UV-vis spectroscopy, joint effect, noncovalent interactions.

Зв'язування двох катіонних сполук з оксидом графену: порівняльний аналіз та спостереження синергічного ефекту. О.А.Боряк, В.С.Шелковський, М.В.Косевич, О.М.Плохотніченко, В.В.Орлов, В.О.Карачевцев

Повідомляється про результати спільної взаємодії двох органічних катіонних сполук, що відрізняються за структурою та характеристиками, а саме бісхетвертинного амонієвого декаметоксина (Dec) з гнучким дикатіоном і метиленового синього (MB) з гетероциклічним пласким катіоном, з оксидом графену (GO) у водній дисперсії. Якісні відмінності у 3D-структурах GO, модифікованого у подвійних (GO+Dec), (GO+MB) та потрійній (GO+Dec+MB) системах, виявлено і описано на підставі UV-vis спектрального аналізу цих систем. При змішуванні компонентів бінарної системи (GO+Dec) спостерігалось досить швидке гелеутворення дисперсії GO. Вигляд бінарної системи (GO+MB) залежав від співвідношення GO до MB: при низькому вмісті GO мала місце індукована

МВ коагуляція ГО у незначні блакитнуваті пластинки з їх наступною седиментацією з часом, тоді як при високому вмісті ГО комплекси ГО з МВ зберігали розчинність у воді. Результати спільного додавання Дек і МВ до дисперсії ГО якісно відрізнялися від описаних вище результатів дії окремих компонентів. При створенні потрібної системи (ГО+Дек+МВ) спостерігалася досить швидка флокуляція всіх компонентів системи, що призводило до утворення темної субстанції, яка спливала до поверхні знебарвленої рідини. У UV-vis спектрах рідкої фази спостерігалася пригнічення ліній усіх компонентів або їх комплексів практично до нульової лінії. Стиснення (ГО+Дек+МВ) композиту до флокул пояснюється відповідністю розмірів катіона МВ і лінкера дикатіона Дек, яка забезпечує щільне заповнення щілин між листами ГО. Ефект флокуляції у системі (ГО+Дек+МВ), що спостерігався, може представляти практичний інтерес при розробці нанокompозитів з сорбційних матеріалів. Інформація про особливості взаємодії ГО з органічними катіонами, що відрізняються за структурою, може бути корисною при вирішенні проблеми доставки ліків.

Сообщается о результатах совместного взаимодействия двух органических катионных соединений, различающихся по структуре и характеристикам, а именно бисчетвертичного аммониевого декаметоксина (Дек) с гибким дикатионом и метиленового синего (МВ) с гетероциклическим плоским катионом, с оксидом графена (ГО) в водной дисперсии. Качественные различия в 3D-структурах ГО, модифицированного в бинарных (ГО+Дек), (ГО+МВ) и тройной (ГО+Дек+МВ) системах обнаружены и описаны на основании UV-vis спектрального анализа этих систем. При смешивании компонентов бинарной системы (ГО+Дек) наблюдалось достаточно быстрое желирование дисперсии ГО. Вид бинарной системы (ГО+МВ) зависел от соотношения ГО к МВ: при низком содержании ГО имела место индуцированная МВ коагуляция ГО в крошечные голубоватые пластинки с их последующей седиментацией со временем, в то время как при высоком содержании ГО комплексы ГО с МВ сохраняли растворимость в воде. Результаты совместного добавления Дек и МВ к дисперсии ГО качественно отличались от описанных выше результатов действия индивидуальных компонентов. При создании тройной системы (ГО+Дек+МВ) наблюдалась достаточно быстрая флокуляция всех компонентов системы, приводящая к образованию тёмной субстанции, всплывающей на поверхность очищенной обесцвеченной жидкости. В UV-vis спектрах жидкой фазы наблюдалось подавление линий всех компонентов или их комплексов практически до нулевой линии. Сжатие (ГО+Дек+МВ) композита до флокул объясняется соответствием размеров катиона МВ и линкера дикатиона Дек, которое обеспечивает плотное заполнение щелей между листами ГО. Наблюдавшийся эффект флокуляции в системе (ГО+Дек+МВ) может представлять практический интерес при разработке нанокompозитов из сорбционных материалов. Информация об особенностях взаимодействия ГО с органическими катионами, различающимися по структуре, может быть полезна при решении проблемы доставки лекарств.

1. Introduction

Within the family of graphene-based nanomaterials [1–6], graphene oxide (GO) [7] attracts noticeable attention presently, since its modification by oxygen-containing functional groups enhances its reactivity in comparison with neat graphene. The main areas of GO application, either current or expected, include biomedical uses [8, 9] connected with biosensing [8], drug delivery [10, 11], antimicrobial [12, 13] and antiviral [14, 15] activity of GO, and ecology-related employments that utilizes GO sorption properties [16–21].

The relevant functioning of GO is based on its noncovalent intermolecular interactions with various organic and inorganic compounds. Traditionally, in model basic studies pair interactions of GO with a single compound are considered. In the real biological and ecological systems, however, a

variety of substances can affect GO at the same time. In the present work we have made an attempt to evaluate the joint effect of at least two different compounds on their interactions with GO in a ternary system. Two organic compounds of cationic nature but of different molecular structure were selected for this purpose: methylene blue (MB) being a planar heterocyclic cation and decamethoxinum (Dec) containing two quaternary ammonium functional groups connected by a flexible polymethylene chain. It was expected that the cationic nature of both compounds would provide their relatively strong coulombic (electrostatic) attraction to partially negative oxygen-containing groups of GO, while any differences, synergism or competition in their interactions with GO might be caused by the structural differences of the cations. Note that both organic salts have the same Cl^-

anion, which avoids taking into account additional effects which may be caused by diverse counterions. Further, both Dec and MB possess antimicrobial properties [22–24] and have been long approved as medicines, which is valuable from the perspective of the current trend of elaboration of graphene and GO functional composites with antimicrobial agents [25, 26].

As to pair systems of GO with the chosen additives, the interaction of bisquaternary ammonium organic salt Dec with GO has not been studied so far. There are two structural features of Dec which distinguish it from amines and ammonium compounds studied earlier: firstly, charging of amines via protonation is pH-dependent and thus changeable, whereas the charge of Dec is permanent; secondly, in contrast to monoalkylammonium compounds, Dec has two separated charged functional groups. Literature data show that different amines and ammonium compounds cause varied effects on GO, which are hard to predict prior to experimental verification. Thus, polyamines, such as diethylenediamine, diethylenetriamine and triethylenetetraamine are utilized to produce GO-based hydrogels [27–31]. Tetraalkylammonium ions (where "alkyl" were methyl, ethyl, propyl and butyl radicals) caused GO exfoliation in aqueous colloidal suspensions and produced layered intercalation structures with GO in the dehydrated state [32]. Cetyltrimethylammonium bromide (CTAB) surfactant assembled on the GO nanosheets surface [33] caused ordered multilamellar stacking of the GO sheets connected by mono- and bilayers of CTAB [34], and recovered GO from aqueous solution by means of froth flotation under ultrasonication [35]. In the recent work [36] a new substance which can be formally referred to as a bisquaternary ammonium compound was synthesized to advance the preparation of GO-based aerogels with enhanced sorption capacity combined with biocidal antibacterial activity valuable for waste water treatment.

Amongst many useful applications of cationic redox-active dye MB [23, 24], its main employment in nanotechnology is connected with the estimation of sorption properties of various nanomaterials [37–40], including GO [7, 41–45]). Note that in these works GO itself was evaluated as a sorbent for removing dyestuff, MB in particular, from the waste water [16–21]. There were reports on MB adsorption on GO in combination with another cationic dye Rhodamine B [20,

46, 47] and preferential adsorption of MB as a cationic dye in comparison with an anionic dye methyl orange on GO [47] along with binding of both cationic and anionic dyes by reduced GO [48]. Possible applications of GO-MB composite as a functional material to make of membranes for water purification were discussed [49].

A popular and self-sufficient method of study of GO interactions, applied in our work, is UV-vis spectroscopy, since binding of various compounds with GO predictably affects the absorption spectra of both GO [50] and the adsorbent. Interestingly, new data on the UV-vis spectroscopic behaviour of MB, MB aggregation effects in particular, continue to appear [51–55] in spite of the apparent completeness of the already accumulated information. In particular, it was reported that at certain conditions MB can be adsorbed at the surface of GO in the form of dimers, trimers and higher aggregates judging from the characteristic changes of the UV-vis spectra of the GO-MB composites [7, 44].

To sum up, the aim of the present work was to investigate the joint effect of two organic cationic salts Dec and MB on their interactions with GO.

2. Experimental

Absorption spectra in the UV-vis range were recorded with the help of Hitachi 356 spectrophotometer (Japan). Quartz cuvettes of 1, 2 or 5 mm width were used. Special tests were performed to verify possible effect of light scattering on UV-vis spectra. The same sample of GO aqueous dispersion was located in the spectrophotometer chamber at the distances of 40 cm or 3 mm from the photomultiplier tube. The scattered light does not reach the detector in the first configuration, while it must fall on detector in the second configuration. No difference was observed in the UV-vis spectra recorded in the both modes, which proves negligible yield of the light scattering to the spectra at the given experimental conditions.

Aqueous solutions of methylene blue and decamethoxinum were mixed with commercial suspension of GO in Eppendorf vessels, stored for a certain period of time, photographed with a digital camera and transferred to quartz cuvettes for spectroscopic measurements.

Chemical structures of organic salts methylene blue and decamethoxinum are presented in Fig. 1.

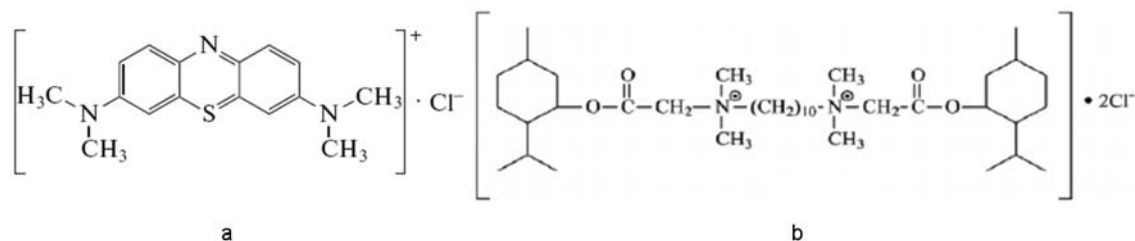


Fig. 1. Chemical structures of organic salts methylene blue (a) and decamethoxinum (b).

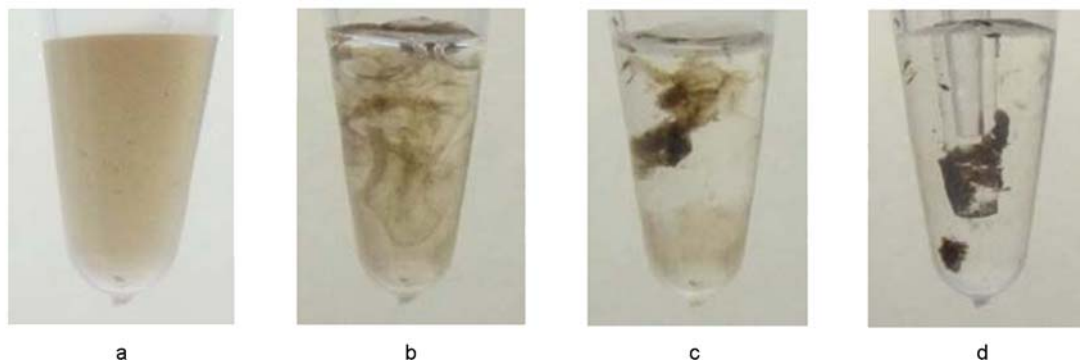


Fig. 2. Transformation of aqueous dispersion of GO (20 μL of 2 $\text{mg}\cdot\text{mL}^{-1}$ in Eppendorf vessel) (a) on addition of Dec ($5\cdot 10^{-2}$ M, 35 $\text{mg}\cdot\text{mL}^{-1}$): (b) — one minute after addition of 5 μL of Dec; (c) — after one minute of mechanical mixing (shaking); (d) assembling of the clot on the plastic pipette tip used for mixing.

Decamethoxinum synthesized in the Institute of Organic Chemistry (Kyiv, Ukraine) and methylene blue produced by OJSC "Vitamins" (Uman, Ukraine) were used in the experiments. Graphene oxide was purchased from GRAPHENEA (San Sebastian, Spain). It contained about 49–56 % of carbon and 41–50 % of oxygen, i.e. the C:O weight ratio is about 1.2–1.3. GO aqueous suspension pH value was 2.

3. Results and discussion

The study of (GO+Dec+MB) ternary system was preceded by testing of binary systems, since (GO+Dec) binary system had not been considered earlier and some fine features of (GO+MB) system required verification.

Binary system (Graphene Oxide + Decamethoxinum). The main effect observed on mixing GO with Dec in aqueous medium was a rather rapid formation of a gel-like dark clot accompanied by the transformation of the initially brownish dispersion of GO (Fig. 2a) into a decolorized transparent supernatant. The rate of these transformations depended on Dec concentration. Dripping a droplet of water solution of Dec with

the concentration higher than 10^{-1} M (70 $\text{mg}\cdot\text{mL}^{-1}$) into GO aqueous suspension caused the latter to assemble almost instantly into a dense dark clot. This differentiated the effect of Dec from that of polyamine compounds, in which case GO gelation took hours.

The separate stages of gel assembling, which are presented in Fig. 2b–d, were observed using Dec solution of somewhat lower concentration of $5\cdot 10^{-2}$ M (35 $\text{mg}\cdot\text{mL}^{-1}$) added to GO of 2 $\text{mg}\cdot\text{mL}^{-1}$ concentration. The homogeneous semi-transparent brownish suspension of GO (Fig. 2a) starts to separate into some dense assemblies right after the water solution of Dec is added (Fig. 2b). Mechanical shaking accelerates the assembling of the floating flakes into a single dense clot (Fig. 2c). Mechanical stirring of the mixture with a plastic pipette tip allows collecting and extracting the clot from the supernatant liquid (Fig. 2d). In terms of physics and chemistry of dispersed systems Dec causes coagulation of aqueous dispersions of GO and gelation of the resulting material.

To evaluate quantitatively the interaction of Dec with GO by means of UV-vis

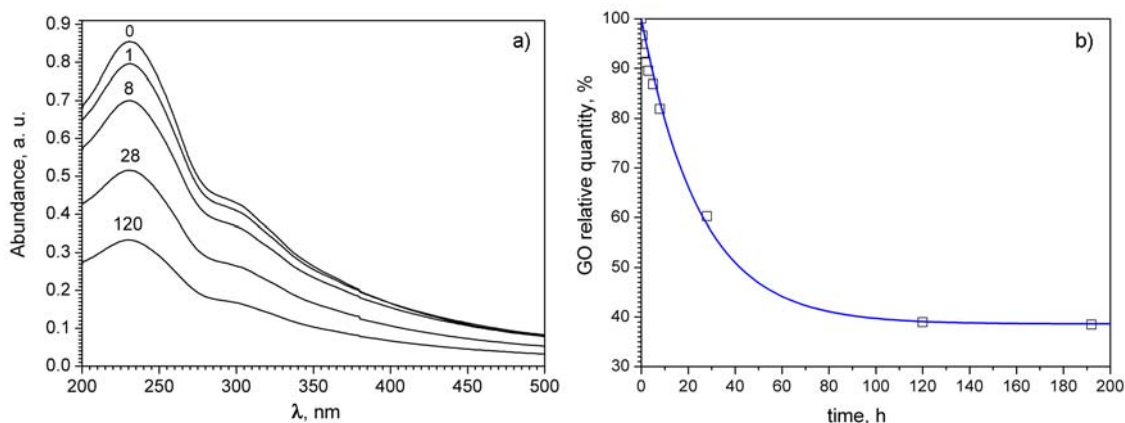


Fig. 3. Changes with time of the mixture of 1.5 mL of GO ($2 \text{ mg}\cdot\text{mL}^{-1}$) with 20 μL of Dec ($1\cdot 10^{-3} \text{ M}$, $0.7 \text{ mg}\cdot\text{mL}^{-1}$) in aqueous medium: a) — time dependence of UV-vis spectra of the supernatant; the time interval starting from the mixing ($t = 0$ hours) is marked above the curves; b) — time dependence of the concentration of GO in the supernatant of the (GO+Dec) system, constructed on the basis of the presented above spectral data.

spectroscopy, lower concentration of Dec of $1\cdot 10^{-3} \text{ M}$ ($0.7 \text{ mg}\cdot\text{mL}^{-1}$) was applied to slow down the gelling process. The task was complicated by the absence of the absorption bands of Dec in the UV-vis range. Therefore it was decided to trace the changes in the spectra of GO. The UV-vis spectra of the supernatant were recorded with the help of a 1 mm wide cuvette at the constant temperature of $+22^\circ\text{C}$.

Fig. 3a shows changes happening to the UV-vis spectra of the aqueous mixture of GO with Dec over time. The appearance of these spectra correlates well with that of GO spectra described in detail in the work [50]. Note that in conformity with the findings of the work [50], the presence of the peak with the maximum at $\lambda = 230 \text{ nm}$ evidences the existence of few-layer (1–3 layers) dispersion of GO, while the transformation of this peak into a smooth shoulder would be a marker of thick-layer dispersions (>10 layers).

The decrease in abundance of the adsorption on the whole, including characteristic band at 230 nm, corresponds to decrease of the content of GO in the liquid phase. Comparison with the data obtained in the work [50] shows that the three-fold decrease in the abundance of the 230 nm band may indicate about 40–50 % decrease in GO concentration. This assumption is supported by the spectra digitization in Fig. 3a by plotting the time (t , h) dependence of the relative GO concentration (I , %) in the supernatant, Fig. 3b. The curve in Fig. 3b can be approximated by exponential dependence:

$$I = A \cdot \exp(-t/T) + B, \quad (1)$$

where $A = 61.4 \text{ (\%)}$, $B = 38.6 \text{ (\%)}$, $T \sim 25 \text{ h}$.

Thus, the dications of Dec provide assembling (coagulation) of GO sheets to gel-like 3D structure. Obviously, two positively charged quaternary alkylammonium moieties in the dication connected by the $(\text{CH}_2)_{10}$ linker can bind together two different sheets of GO via electrostatic interactions with oxygen-containing groups of GO, bearing partially negative charge. Our previous estimates show that the distance between the centers of the positive charges location in the most extended conformation of the $(\text{CH}_2)_{10}$ polymethylene chain linker is about 1.4 nm [56]. Since the interlayer distance of GO is estimated as 0.5 nm [50], the separation of GO sheets or flakes to larger distances in the GO-Dec complexes provides the openwork structure of the gel formed due to noncovalent Dec binding.

On the other hand, the role of GO is in trapping of Dec dications from solution, that is purification of water from this quaternary ammonium compound if it is regarded as an ecological pollutant. The dications trapped within the GO clot cannot be freely released via dissociation in aqueous medium, which provides the stability of the 3D structure and retention of the Dec by GO for a long time (at least 100–120 h, as shown in Fig. 3a). It was shown in our previous works [57, 58] that Dec dication tends to substitute readily its inorganic chlorine counterion for an anion of organic acids.

Similarly, quaternary ammonium groups of Dec can form salt bridges with COO^- anionic moieties of GO.

The effect observed is to be accounted in investigations connected with the popular subject of drug delivery. On the one hand, relatively strong electrostatic binding of medicinal compounds containing quaternary alkylammonium groups with GO is expected. On the other hand, in the living systems biomolecules possessing alkylammonium functional groups may be able to trap GO flakes inserted into such systems.

Composites of GO with polycations and quaternary ammonium salts possessing antimicrobial activity are currently an emerging and urgent object for synthesis and characterization; however, there is still a limited number of publications on this subject [25, 26, 36]. Our present results show that bisquaternary ammonium salt decamethoxinum already approved as an antimicrobial agent can be utilized in production of GO-based functional gels.

From point of view of the aim of the present study it should be noted that in the previous investigations of interactions of quaternary ammonium modified GO with other compounds, preformed GO composites processed by drying, freeze-drying, sonication, purification were utilized as new individual materials, while joint interactions of pristine GO with a quaternary ammonium and some other compound in a ternary system were not paid proper attention.

Binary system (Graphene Oxide + Methylene Blue). It is known that on examination of finely dispersed materials, namely MB is often engaged as a test compound for evaluation of their adsorption properties. Interactions of MB with graphite-based nanomaterials, including GO, were repeatedly considered in the literature in relation to various tasks [11, 17, 19, 37–40, 41–44]. Here we have probed the (GO+MB) pair system as a necessary step for further ternary (GO+Dec+MB) system evaluation at the same conditions. Since in the framework of our task we needed confident differentiation of the effects caused by addition of the single or the pair of additives to GO, we had to systematize all possible changes in the UV-vis spectra inflicted by MB to GO dispersion.

With this purpose we had tried relatively wide range of GO to MB ratios and have determined the ranges of the most noticeable changes in the samples appearance accompanied by the related changes in their

UV-vis spectra. To obtain the concentration dependences, $10 \mu\text{g}\cdot\text{mL}^{-1}$ aqueous stock solution of MB was divided in several equal portions which were doped by increasing amounts of GO providing a set of GO concentrations in the system growing gradually from 6 to $98 \mu\text{g}\cdot\text{mL}^{-1}$. Value pH of these systems decreased from 7.5 to 4.6, while pH of the initial GO dispersion was 2.0.

It should be noted at once, that heterocyclic planar cation of MB caused qualitatively different effect on GO dispersion as compared to extended flexible Dec dication: expectedly, no gelation of GO occurred in the presence of MB; formation of tiny solid flakes took place instead.

It was observed that in dependence of MB to GO ratio the aqueous suspensions either show precipitation within a day of storage or may remain stable. To evaluate roughly the composition of the insoluble sediment, an expedient absent in previous works was applied: the UV-vis spectrum of the liquid phase (supernatant) recorded after 24 h of the sample storage was subtracted from that recorded right after (within 10 min) the components mixing. The full set of the data obtained will be published elsewhere, and here we describe the major transformations of the UV-vis spectra of the studied systems (Fig. 4). Since the main changes are expected for MB component of the integral UV-vis spectrum of (GO+MB) system, the spectrum of the initial MB solution is presented for reference in all parts of Fig. 4 (dotted blue line). Its characteristic reference features described in the early basic works [39, 40] are the bands attributed to free MB monomer cation, maximum at $\lambda = 664 \text{ nm}$, and MB dimer, maximum at $\lambda = 605 \text{ nm}$. GO line similar to that presented in Fig. 2 with the maximum at $\lambda = 230 \text{ nm}$ is merged with the line of MB in the spectra of (GO+MB) system and its contribution grows continuously with the increase of GO content in the samples. The qualitative changes in the (GO+MB) system occur in conventionally three ranges of GO to MB ratios.

In the first range with relatively low content of GO ($6\text{--}16 \mu\text{g}\cdot\text{mL}^{-1}$) in the system the behavior of the set of samples was similar: right after the addition of GO to MB solution tiny bluish flakes appeared in the liquid and remain suspended for several hours; however, they precipitated as visible blue aggregates after a day of storage at ambient conditions. The UV-vis spectra of the samples in this range demonstrate simi-

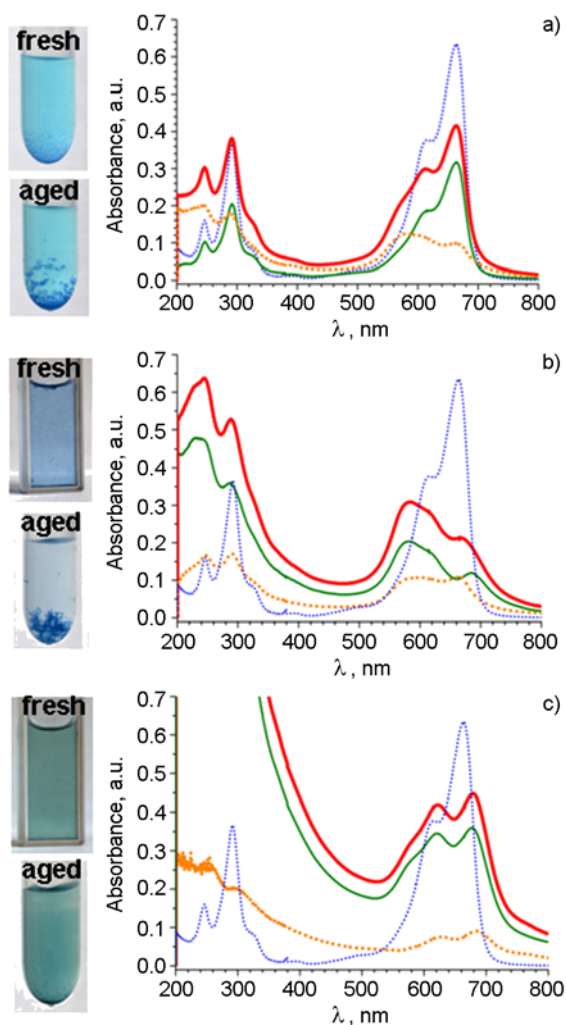


Fig. 4. (Colour in the online version). Transformations of the appearance of binary (GO+MB) system (left column) and the corresponding UV-vis spectra (right column) in dependence of the GO to MB ratio. The spectrum of the initial MB aqueous solution ($10 \mu\text{mL}^{-1}$) is shown for reference (dotted blue line). GO concentration in the samples is $8 \mu\text{mL}^{-1}$ (a), $25 \mu\text{mL}^{-1}$ (b); $98 \mu\text{mL}^{-1}$ (c). Solid red lines — the spectra recorded right after the addition of GO to MB ("fresh" solution); thin green lines — 24 hours of aging of the (GO+MB) system; dashed orange lines — the result of subtraction of the spectrum of the "aged" sample from the spectrum of freshly prepared mixture, which nominally reflects the composition of the sediment.

lar trends illustrated by Fig. 4a. In the spectrum of the just mixed components (solid red line) the expected adsorption of MB on GO causes noticeable decrease of the MB monomer band. At the same time the

abundance of the MB dimer increases in relation to that of the monomer, and a shoulder at $\lambda = 570 \text{ nm}$ appears and grows in abundance with increase of GO content in the sample. This band is attributed to MB trimers and higher aggregates, adsorbed at the dispersed material [39]. Since low quantity of GO is unable to absorb all MB from solution, the total spectrum in the visible range must correspond to superposition of the spectra of unbound MB and MB bound in GO-MB complexes floating in solution. After a day of storage the spectrum of the supernatant (thin green line) becomes qualitatively similar to that of neat (unbound) MB. The difference between the spectra of the fresh and aged samples (dashed orange line) must reflect the composition of the material gone to the precipitate. This differential spectrum is dominated by the band of the adsorbed MB trimers ($\lambda = 570 \text{ nm}$) obviously fused with the band of adsorbed dimers ($\lambda = 596 \text{ nm}$ [39]); the band of the monomer is suppressed. The band of GO at $\lambda = 230 \text{ nm}$ disappears from the spectrum of the supernatant and reappears in the nominal spectrum of the precipitate. We can speculate that MB, being in excess, is adsorbed at the flakes of GO forming dimers, trimers and, virtually, higher aggregates. Separate flakes of GO covered with MB tend to aggregate; the extent of aggregation increases with time resulting eventually in the visible particles precipitation. The driving force of the GO-MB composite precipitation is the neutralization of the negative charge of GO by MB cations (measured pH values for this range were 7.5–7.0).

In the second range with some "medium" content of GO in the system ($25\text{--}36 \mu\text{g}\cdot\text{mL}^{-1}$) noticeable changes of the sample appearance take place (Fig. 4b). Larger quantity of GO enables more efficient adsorption of MB from solution, which is reflected in strong decrease of MB monomer peak both in the freshly prepared (solid red line) and aged (thin green line) systems. The merging band of the adsorbed dimers, trimers and higher aggregates becomes dominant in the spectrum and exceeds the band of the monomers. Interestingly, this wide band is preserved in the spectrum of the supernatant of the day aged sample; it is present in the spectrum of the "precipitate" (dashed orange line) as well.

In the third range with high GO content (concentrations higher than $50 \mu\text{g}\cdot\text{mL}^{-1}$, $\text{pH} < 5$) dramatic alteration takes place

caused obviously by the changes in the type of MB adsorption, which lead to re-gaining of solubility by GO-MB composite. In the photographs in Fig. 4c the turbid character of the (GO+MB) suspension can be seen; the liquid phase has a green tint which may emerge due to mixing yellow-brown colour of GO and blue colour of MB. The look of suspension is the same for the fresh and aged samples; no visible precipitation is observed. This is reflected in practical coincidence of the shape and abundance of the spectral curves of the freshly prepared (solid red line) and aged (thin green line) samples and noticeable suppression of the "precipitate" spectrum (dashed orange line). At the same time the structure of the MB-related bands undergo qualitative changes. The band of the MB monomer grows in abundance, but now it becomes definitely red-shifted to $\lambda = 673$, which is attributed to the adsorbed MB monomers [39] (at the GO surface in this case). The abundance of such monomers becomes roughly equal to that of dimers and trimers. There is no distinguishable peak of the unbound MB monomer, which may mean that all MB is adsorbed by GO. It may be speculated, that at relatively high content of GO the content of MB becomes insufficient for multi-layer coverage of GO flakes; the MB aggregates do not form and MB cations are distributed as monomers over the GO surface. In such case the system is no longer neutral, pH value of the sample becomes acidic and GO-MB composite flakes regain the soluble character. There seems to be some paradox: it may be expected that higher quantity of GO will remove MB from the liquid more efficiently. In reality, although more MB is bound to GO, it is retained in the liquid within GO-MB complexes which do not precipitate.

Interestingly, the spectroscopic features similar to the described above were observed for GO interactions with Pyronin Y, which is a structural analogue of MB with sulfur atom substituted by oxygen atom [59].

As to the mechanisms of MB cations interactions with GO, various types of noncovalent intermolecular interactions can be involved, as described in the literature [48, 21]: van-der-Waals and hydrophobic interactions on MB stacking with oxygen-deficient graphite-like areas [60] of GO, π - π interactions, hydrogen bonding with oxygen-containing functional groups, and coulombic attraction. Recently the results of molecular dynamics simulation of MB interaction with

GO in water were published [47, 61–63], which showed mainly planar stacking of the MB monomer with GO plane. However, relatively small area of GO sheets and involvement of a limited number of MB cations used in these simulations did not permit to model the real wide range of GO to MB ratios, when either MB aggregates cover densely GO surface or single monomers are distributed over the extended area of GO. A suggestion concerning alignment of the MB aggregates in orthogonal (vs stacked) orientation in relation to the GO surface plane is expressed in some works [42, 44]; its verification necessitates further investigations.

For further discussion of the ternary system it is important, that the complexes of MB with GO sheets in the binary system continue to float in the suspension after their assembling and observation of UV-vis spectra of this system is possible. The alternative may be in complete sedimentation of the GO-MB complexes resulted in suppression of the corresponding UV-vis spectrum, which does not happen at any GO to MB ratio.

Ternary system (Graphene Oxide + Decamethoxinum + Methylene Blue).

Finally, the main object of our study, that is the ternary system containing GO with two different organic cations, Dec and MB, was prepared and investigated.

Three possible ways of creation of the ternary system by mixing of aqueous dispersions of GO (180 $\mu\text{g}\cdot\text{mL}$) with two other components were applied:

- 1 — {(GO+Dec)+MB} — Dec (20 $\mu\text{g}\cdot\text{mL}$) added first followed by MB (10 $\mu\text{g}\cdot\text{mL}$);
- 2 — {(GO+MB) + Dec} — MB (10 $\mu\text{g}\cdot\text{mL}$) added first followed by Dec (14 $\mu\text{g}\cdot\text{mL}$);
- 3 — {GO+(MB+Dec)} — performed mixture of MB and Dec (7 + 14 $\mu\text{g}\cdot\text{mL}$) was added to GO suspension. Here final concentrations of the components in the mixture are marked.

The results of adding the first component, naturally, were the same as established above for the binary (GO+Dec) and (GO+MB) systems. On addition of the second component or the two components at once rapid (within several minutes) dramatic changes in the sample appearance took place after gentle shaking of the vessel, producing qualitatively the same final result shown in the insert in Fig. 5c, namely, flocculation and surfacing of the interaction product. In the course of formation of {(GO+Dec)+MB} ternary system the liquefaction of the brownish gel particles of the

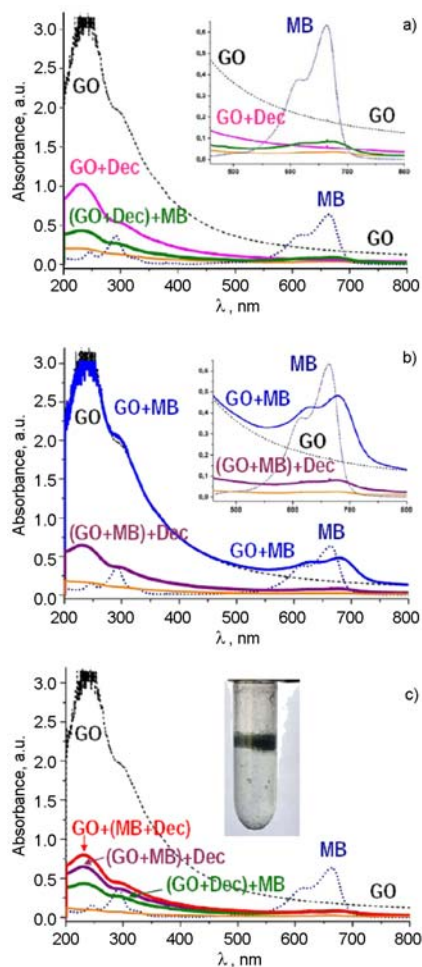


Fig. 5. (Colour online). UV-vis characterization of the ternary (GO+Dec+MB) system formation. Reference spectra of pristine GO suspension (180 $\mu\text{g}\cdot\text{mL}$) (black dashed line) and solution of MB (dark blue dotted line) are shown in all sets. Part a: magenta line — the result of addition of Dec (20 $\mu\text{g}\cdot\text{mL}$) to GO; green line — subsequent addition of MB (10 $\mu\text{g}\cdot\text{mL}$) to (GO+Dec) mixture. Part b: blue line—result of addition of MB (10 $\mu\text{g}\cdot\text{mL}$) to GO; violet line — subsequent addition of Dec (14 $\mu\text{g}\cdot\text{mL}$) to (GO+MB) mixture. Part c: red line — addition of the mixture of (Dec+MB) to GO; two lines beneath are reproductions of lines of ternary systems from parts (a) and (b) for comparison. The spectra of the binary mixtures are recorded just after the addition of the first component; the spectra of the ternary mixtures are obtained within 10 min after the addition of the second component. Thin orange line in all parts is the spectrum recorded for ternary systems after 24 h storage. The appearance of the ternary system exhibiting flocculation effect is shown in the insert in part c.

(GO+Dec) component and discoloration of the added MB component occurred; the resulting liquid became practically transparent, while black or dark blue flocs floated and aggregated at the surface region of the liquid. In the case of preparation of $\{(GO+MB)+Dec\}$ system the bluish turbid suspension of solubilized (GO+MB) (similar to that shown in Fig. 4c) turned to transparent and colourless liquid; again, some dark residue was assembled at the top of the liquid. On addition of the mixture of two cationic compounds at once, the same rather rapid transformation of GO suspension took place resulting in separation of the sample to practically transparent colourless liquid and surfacing dark substance.

The changes in the appearance of the samples in the course of formation of the ternary system were reflected in the consistent dramatic changes in their UV-vis spectra, Fig. 5. The spectra of pristine suspension of GO (black dashed line) and solution of neat MB (dark blue dotted line) are shown for reference in all parts of the Fig. 5.

On addition of Dec as the first additive, general subsidence of the GO line including three-fold decrease of the abundance of characteristic GO peak at 230 nm took place within several minutes (magenta line in Fig. 5a), corresponding to involvement of GO into gel particles. On addition of MB as the first additive in the concentration ensuring formation of suspension of MB-modified GO, the spectrum (blue line in Fig. 5b) was similar to that in Fig. 4c for the binary (GO+MB) system.

Addition of MB as the second component to (GO+Dec) system caused rapid two-fold decrease of the GO peak at 230 nm (green line in Fig. 5a); in total ten-fold decrease of the initial abundance of pristine GO took place; the peaks characteristic of MB did not show in the spectra at all.

Addition of Dec as the second component to (GO+MB) system caused rapid six times fall of the GO peak at 230 nm and practical disappearance of the MB characteristic peaks (violet line in Fig. 5b).

Addition of the mixture of (MB+Dec) to GO suspension caused the same result (red line in Fig. 5c) as the stepwise addition of the two separate components, which is demonstrated by comparison of this line with the lines corresponding to ternary systems in Figs. 5a, b for the two previous cases, collected in Fig. 5c.

The spectra of the binary systems are recorded right after the addition of the first

component; the spectra of ternary systems are obtained within 10 min after the addition of the second component. The results of subsequent measurement made after 4, 20 and 24 h (the latter shown as thin orange lines in Fig. 5a–c) demonstrated continuous decrease in abundance. The recession of the spectral lines practically to the baseline pointed to further withdrawal of all components from the supernatant.

Visual transformations of the samples mirrored by their UV-vis spectra demonstrated that the mutual effect of two cationic organic compounds on GO, independently of the order of their admission to the system, is the same and differed qualitatively from the effects of each single component. From the point of view of colloidal chemistry and physics of dispersed systems the effect can be referred to as flocculation.

The visual discoloration of the supernatant of the (GO+Dec+MB) system supported by the disappearance of MB characteristic peaks from the spectrum of the liquid phase unequivocally confirmed total inclusion of MB into the GO composite formed. While the spectra in Fig. 5a did not permit to exclude a possibility of substitution of Dec by MB in the ternary mixture, the transformation of the spectra in Fig. 5b confirm binding of soluble MB-covered GO flakes by Dec resulting in their removal from suspension. There is no signs of selective adsorption of a definite cationic component by GO from the (Dec+MB) mixture as well.

Obviously, the composite complexes formed in the ternary (GO+Dec+MB) system preserve both types of Dec and MB cations; the structure of such composites necessitates further investigations and modeling. At the present stage we can make some assumptions only. It may be expected, that the (GO+Dec) gel, similarly to hydrogels formed by polyamines and GO [27–31], would efficiently adsorb MB dye from solution; in this case the structure of the gel "filled" by MB might be preserved. In practice, however, we observe compression of the gel structure to flakes/flocs which occupy much smaller volume than the initial gel. At the same time soluble flakes of (GO+MB) complexes (in the second sample) are assembled by Dec and removed from suspension.

It may be speculated that the separation of GO sheets linked by two charged groups of the Dec dication parted by 1.4 nm (the distance between two quaternary nitrogen

atoms [22]) provides gaps (cavities, confined spaces) required/sufficient for intercalation of a set of MB cations. The MB species adsorbed at two adjacent GO sheets (linked by Dec) may tend to form aggregates causing collapse of the sheets, which is not hampered by decamethoxinum link due to flexibility of its interchange chain. Remains of water molecules are repelled from the collapsing cavities and thus the volume of the new ternary composite (GO+Dec+MB) becomes reduced in comparison with the binary (GO+Dec) structure. In the case of addition of Dec to (GO+MB) suspension the flexible dications "seal" the (GO+MB) flakes and assemble them to larger structures.

While loose bulk 3D structure of the GO composites with polyamines and quaternary ammonium compounds is provided by chaotic binding of GO sheets by the gelling agents, the compression of the gel mesh (crosslinked by Dec dications) by MB must be due to some ordering effect, which cannot be achieved by simple filling of the random gel cavities by uneven stacks of MB cations. As it was already mentioned above, the available literature data [61–63] on modeling of interaction of a limited number of MB cations with a relatively small GO sheet demonstrate mainly stacking location of MB monomer heterocycles over the GO plane and do not describe adsorption of MB as trimers and higher aggregates. Alternatively, it may be suggested that in accord with assumptions made in the works [42, 44] the aggregates at the GO surface are formed by MB heterocycles arranged themselves orthogonal to the GO plane. It can be speculated further that namely the orthogonal arrays of MB may connect two adjacent GO sheets; the uniform distance between the sheets provided by the arrays of MB cations may flattened the fluted structure of GO sheets resulting in their space compactization. Smearing of the positive charge over the MB cation [64] may provide its simultaneous electrostatic attraction to two GO sheets by two terminal — $\text{N}(\text{CH}_3)_2$ groups similarly to the "true" (Dec) dications. Approximate concordance of the length of the interchange linker in the Dec dication (1.4 nm) and the "length" of the MB cation (1 nm distance between two nitrogen atoms) may facilitate orthogonal packing of MB aggregates in the gap between two GO sheets, which width is fixed by the Dec dication in the flocs of the ternary (GO+Dec+MB) composite.

The feature of Dec as a surfactant may facilitate the surfacing of the flocs [35]. It is worth noting that the flocculation in the (GO+Dec+MB) system occurred more rapidly (practically instantaneously) in comparison with the systems with other polyamines and quaternary ammonium salts described in the literature. This finding shows the direction for further design of the efficient flocculating dications with the intercharge distances tailored for a specific adsorbent. Further, Dec is a simpler water-soluble organic compound than other polymeric substances (e.g. polyacrylamide, gelatin) usually utilized as flocculating agents, that points to a possibility of testing of other bisquaternary ammonium agents as more cheap and efficient flocculants. In addition, antimicrobial and antiseptic properties of Dec are a precious supplement in Dec-containing composites.

Obviously, delocalization or smearing of the single positive charge over a number of atoms of the both MB^+ [64] and Dec^{2+} [22] cations, demonstrated in our previous works, diminishes the coulombic repulsion between the charges of the same sign inherent to two different organic cations and permits them to coexist in the (GO+Dec+MB) composite. This issue necessitates further investigations in a stream of recent interest in the subject of cation-cation interactions [65]. The stabilizing role of Cl^- anions is to be considered as well.

It is interesting, that two different properties of Dec are exhibited under different conditions: in the two-component (GO+Dec) system the Dec as a dication linking GO sheets causes gelation of the GO-Dec composite, while in the ternary system Dec property of a surfactant promotes flocculation of GO-MB flakes and the gel structure is destroyed or does not form at all. In other terms MB prevents gelation of GO by Dec.

Practical implications of the findings of this work may be as follows. Firstly, non-additive result of formation of GO with two different cations may be accounted during elaboration of GO composites. Secondly, finding of a pair of cations, which facilitates their more efficient removing from the liquid by GO in comparison with removing of each single component, opens the way to search of other specific combinations of this kind. Assembling of the (GO+Dec+MB) to a separate phase leaving practically clean supernatant eliminates the need in further purification of the liquid. Thirdly, the ef-

fect of GO interactions with cations of different nature must be accounted on development of biomedical materials and drug delivery systems. Namely, possible interactions of GO or drug-loaded GO with charged groups of biomolecules must be thoroughly analyzed.

4. Conclusions

The fulfilment of the main task of the investigation, consisting in evaluation of the joint action of two organic cationic salts of different structure and nature (Dec and MB) on their interactions with GO, resulted in observation of the efficient flocculation effect in the ternary (GO+Dec+MB) aqueous system, that is surfacing of the dark compact residue over the purified decolorized liquid. The result was the same independently of the order of addition of organic salts to GO suspension. The removing of all solutes and dispersed particles from the liquid was evidenced by the suppression of the characteristic UV-vis spectra of the components practically to the baseline.

Such behaviour of the ternary (GO+Dec+MB) system differed qualitatively from the phenomena inherent to the binary systems: formation of the gel clot was observed on mixing of GO dispersion with Dec solution, while a turbid suspension or dark visible flakes was formed in the GO mixtures with MB. Thus, the coulombic interaction between the cations and GO is only the tool for attraction of the components, while the difference in 3D structures of (GO+Dec) and (GO+MB) composites are determined by the distinctions in the structure of Dec and MB cations.

A proposed idea concerning the reasons and mechanisms of the synergic action of the two cationic compounds assumed the matching of the intercharge distance in the Dec dication connecting two GO sheets with linear size of MB cations, which permits filling of the inter-sheet spaces by MB aggregates.

The observed effects accompanying formation of the composite (GO+Dec+MB) with two cationic additives may be accounted in development of functional GO-based composite materials destined, in particular, for water purification. As to a problem of GO applications in drug delivery, a possibility of varied types of interaction of GO with different cationic functional groups of biomolecules are to be thoroughly analyzed.

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