Full Paper ____ *Thematic Section:* Preparative Research.
The Reference Object Identifier – ROI: jbc-01/20-62-4-12 *Subsection:* Organic Chemistry.
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/20-62-4-12
Submitted on April 29, 2020.

Hybrid system «layered magnesium silicate – chlorin e_6 13(1),15(2),17(3)-*N,N′,N″*-(2-hydroxyethyl)triamide»

© **Inna V. Loukhina**,[+] **Irina S. Khudyaeva**, and **Dmitry V. Belykh***
Institute of Chemistry of Komi Science Centre of the Ural Branch of the Russian Academy of Sciences. Pervomaiskaya St., 48. Syktyvkar, 167000. Republic of Komi. Russia. Phone: +7 (8212) 21-99-47.
E-mail: loukhina-iv@chemi.komisc.ru, belykh-dv@mail.ru

*Supervising author; [+]Corresponding author
Keywords: chlorin e_6, chlorin e_6 derivatives, layered magnesium silicate.

Abstract

Matrices based on layered silicates have a set of useful properties, in particular, they are able to increase the stability and photosensitizing ability of porphyrins. Hybrid systems “layered silicate - porphyrin (metal porphyrin)” are promising as active components of systems for light collecting and artificial photosynthesis, catalysts, photocatalysts. The hybrid systems with content of $1.4 \cdot 10^{-6}$ and $4.2 \cdot 10^{-6}$ mol of the chlorin *e6* 13(1),15(2),17(3)-*N,N′,N″*-(2-hydroxyethyl)triamide per 1 g of layered magnesium silicate was obtained by heat treatment method of a synthetic layered magnesium silicate of hectorite composition when treated with an aqueous-alcoholic solution of organic component. The molar ratio of the starting components is: $Mg(OH)_2$: SiO_2 : LiF = 1 : 1.51 : 0.25 : chlorin *e6* derivative = 1 : 1.51 : 0.25 : ($19.93 \cdot 10^{-5}$ – $59.58 \cdot 10^{-5}$). Using dynamic light scattering and laser Doppler electrophoresis, it was shown that the introduction of chlorin *e6* 13(1),15(2),17 (3)-*N,N′,N″*- (2-hydroxyethyl) triamide leads to the growth of hybrid particles (162 ± 3 nm) and a decrease in their aggregative stability (-30 ± 1 mV), compared with the initial layered magnesium silicate (133 ± 1 nm, -33 ± 1 mV). In this case, the introduction of more hydrophilic chlorin *e6* 13(1),15(2),17(3)-*N,N′,N″*-(2-hydroxyethyl)triamide, in the molecule of which there are three fragments of ethanolamine, allows to obtain smaller hybrid particles (162 ± 3 nm), compared with hybrid particles (248 ± 6 nm) formed by the action of chlorin *e6* 13(1),17(3)-*N,N′*-(2-hydroxyethyl)diamide15(2)-methyl ether, in the molecule of which there are two fragments of ethanolamine. Using the methods of X-ray phase analysis and electron spectroscopy in the UV-visible region, it was found that individual molecules of chlorin *e6* 13(1),15(2),17(3)-*N,N′,N″*-(2-hydroxyethyl)triamide were sorbed on the surface of silicate particles due to the electrostatic interaction between the protonated molecules of the macrocycle and the ionized hydroxyl groups of magnesium silicate. It was shown that the higher hydrophilicity of chlorin *e6* 13(1),15(2),17(3)-*N,N′,N″*-(2-hydroxyethyl)triamide, compared with chlorin *e6* 13(1),17(3)-*N,N′*-(2-hydroxyethyl)diamide15(2)-methyl ether did not contribute to the intercalation of the organic component into the interlayer space of layered magnesium silicate under the conditions of a water-alcohol medium.

References

[1] K.V. Efimov, L.Yu. Tsareva, N.F. Ushmarin, N.I. Koltsov Influence of magnesium hydrosilicate on the properties plantar rubber. *Butlerov Communications*. **2020.** Vol.60. No.1. P.91-95. DOI: 10.37952/ROI-jbc-01/20-61-1-91
[2] N.A. Zherdetsky, N.U. Shlyahtin, S.B. Romadenkina, T.V. Aniskona. The influence of process parameters of the cracking thermoplastic polymers to yield products. *Butlerov Communications.* **2018.** Vol.56. No.10. P.123-126. DOI: 10.37952/ROI-jbc-01/18-56-10-123
[3] R.E. Grim. Clay Mineralogy. *New York: McGraw-Hill.* **1953**. 384p.
[4] M. Ogawa, R. Takee, Y. Okabe, Y. Seki. Bio-geo hybrid pigment; clay-anthocyanin complex which changes color depending on the atmosphere. *Dyes and Pigments.* **2017**. Vol.139. P.561-565. https://doi.org/10.1016/j.dyepig.2016.12.054.
[5] G. Cidonio, C.R. Alcala-Orozco, K.S. Lim, M. Glinka, I. Mutreja, Y.-H. Kim, J.I. Dawson, T.B.F. Woodfield, R.O.C. Oreffo. Osteogenic and angiogenic tissue formation in high fidelity nanocomposite Laponite-gelatin bioinks. *Biofabrication.* **2019**. Vol.11. No.3. 035027. https://doi.org/10.1088/1758-5090/ab19fd.
[6] S.(G.) Intasa-ard, M. Ogawa. Layered Silicates as a Possible Drug Carrier. *The Enzymes.* **2018.** Vol.44. Ch.7. P.117-136. https://doi.org/10.1016/bs.enz.2018.08.003
[7] M. Roozbahani, M. Kharaziha, R. Emadi. pH sensitive dexamethasone encapsulated laponite nanoplatelets: Release mechanism and cytotoxicity. *International Journal of Pharmaceutics.* **2017**. Vol.518. No1-2. P.312-319. https://doi.org/10.1016/j.ijpharm.2017.01.001.

[8] T.J. Dening, N. Thomas, S. Rao, C. van Looveren, F. Cuyckens, R. Holm, C.A. Prestidge. Montmorillonite and Laponite Clay Materials for the Solidification of Lipid-Based Formulations for the Basic Drug Blonanserin: In Vitro and in Vivo Investigations. *Molecular Pharmaceutics.* **2018**. Vol.15. No.9. P.4148-4160. https://doi.org/10.1021/acs.molpharmaceut.8b00555

[9] S.S. Das, Neelam, K. Hussain, S. Singh, A. Hussain, A. Faruk, M. Tebyetekerwa. Laponite-based Nanomaterials for Biomedical Applications: A Review. *Current Pharmaceutical Design.* **2019**. Vol.25. No.4. P.424-443. https://doi.org/10.2174/1381612825666190402165845.

[10] M.C. Da Rocha, E.M.deA. Braz, L.M.C. Honório, P. Trigueiro, M.G. Fonseca, E.C. Silva-Filho, S.M. Carrasco, M.S. Polo, C.V. Iborra, J.A. Osajima. Understanding the effect of UV light in systems containing clay minerals and tetracycline. *Applied Clay Science.* **2019**. Vol.183. P.103-109. https://doi.org/10.1016/j.clay.2019.105311.

[11] T. Thiebault. Raw and modified clays and clay minerals for the removal of pharmaceutical products from aqueous solutions: State of the art and future perspectives. *Critical Reviews in Environmental Science and Technology.* **2020**. Vol.50. No.14. P.1451-1514. https://doi.org/10.1080/10643389.2019.1663065.

[12] T. Thiebault, M. Boussafir. Adsorption Mechanisms of Psychoactive Drugs onto Montmorillonite. *Colloid and Interface Science Communications.* **2019**. Vol.30. 100183. https://doi.org/10.1016/j.colcom.2019.100183.

[13] B. Biswas, L.N. Warr, E.F. Hilder, N. Goswami, M.M. Rahman, J.G. Churchman, K. Vasilev, G. Pan, R. Naidu. Biocompatible functionalisation of nanoclays for improved environmental remediation. *Chemical Society Reviews.* **2019**. Vol.48. No.14. P.3740-3770. https://doi.org/10.1039/c8cs01019f.

[14] M. Nowakowska, K. Szczubiałka. Photoactive polymeric and hybrid systems for photocatalytic degradation of water pollutants. *Polymer Degradation and Stability.* **2017**. Vol.145. P.120-141. https://doi.org/10.1016/j.polymdegradstab.2017.05.021.

[15] L. Le Forestier, F. Muller, F. Villieras, M. Pelletier. Textural and hydration properties of a synthetic montmorillonite compared with a natural Na-exchanged clay analogue. *Applied Clay Science.* **2010**. Vol.48. No.1-2. P.18-25. https://doi.org/10.1016/j.clay.2009.11.038.

[16] B.-S. Yu, Y.-Y. Liu. Improvement in phase purity and yield of hydrothermally synthesized smectite using Taguchi method. *Applied Clay Science.* **2018**. Vol.161. P.103-109. https://doi.org/10.1016/j.clay.2018.04.001.

[17] A. Ishii, T. Itoh, H. Kageyama, T. Mizoguchi, Y. Kodera, A. Matsushima, K. Torii, Y. Inada. Photostabilization of chlorophyll a adsorbed onto smectite. *Dyes and Pigments.* **1995**. Vol.28. P.77-82. https://doi.org/10.1016/0143-7208(95)00005-Z.

[18] T. Fujimura, T. Shimada, S. Hamatani, S. Onodera, R. Sasai, H. Inoue, S. Takagi. High Density Intercalation of Porphyrin into Transparent Clay Membrane without Aggregation. *Langmuir.* **2013.** Vol.29. No.16. P.5060-5065. https://doi.org/10.1021/la4003737.

[19] I.V. Loukhina, I.S. Khudyaeva., A.Yu. Bugaeva, B.N. Dudkin and D.V. Belykh. Modification of Magnesium Silicate with 15(2)-Methyl Ester of 13(1),17(3)-Diamino-N,N'-bis(2-hydroxyethyl)-13(1),17(3)-dioxochlorin e_6. *Russian Journal of General Chemistry*. **2017**. Vol.87. No.5. P.912-917. https://doi.org/10.1134/S1070363217050036

[20] I.V. Loukhina, I.S. Khudyaeva, A.Yu. Bugaeva, D.V. Belykh. Hybrid system «layered magnesium silicate – chlorin e_6 13(1), 17(3)-N,N'-(2-hydroxyethyl)diamide 15(2)-methyl ester». *Butlerov Communications.* **2019.** Vol.58. No.4. P.34-39. DOI: 10.37952/ROI-jbc-01/19-58-4-34

[21] D. Gryglik, J.S. Miller, S. Ledakowicz. Solar energy utilization in degradation of 2-chlorophenol by immobilized photosensitizers. *Solar Energy.* **2004**. Vol.77. P.615-623. https://doi.org/10.1016/j.solener.2004.03.029.

[22] D. Drozd, K. Szczubiałka, M. Kumorek, M. Kepczynski, M. Nowakowska. Photoactive polymer – nanoclay hybrid photosensitizer for oxidation of phenol in aqueous media with the visible light. *Journal of Photochemistry and Photobiology A: Chemistry.* **2014**. Vol.288. P.39-45. https://doi.org/10.1016/j.jphotochem.2014.04.025.

[23] D.V. Belykh, L.P. Karmanova, L.V. Spirikhin, A.V. Kuchin. Synthesis of amide derivatives of chlorin e_6. *Russian Journal of Organic Chemistry*. **2007**. Vol.43. No.1. P.126-134. https://doi.org/10.1134/S1070428007010174

[24] M. Ogawa, T. Matsutomo, T. Okada. Preparation of hectorite-like swelling silicate with controlled layer charge density. *Journal of the Ceramic Society of Japan*. **2008**. Vol.116. No.12. P.1309-1313. https://doi.org/10.2109/jcersj2.116.1309.

[25] K.A. Carrado, R.E. Winans. Interactions of Water-Soluble Porphyrins and Metalloporphyrins with Smectite Clay Surfaces. *Chemical Materials*. **1990**. Vol.2. P.328-335. https://doi.org/10.1021/cm00009a027.