

Hybrid system «layered magnesium silicate – chlorin e₆ 13(1), 17(3)-N,N'-(2-hydroxyethyl)diamide 15(2)-methyl ester»

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Abstract

Hectorite type layered magnesium silicate have been synthesized by heat treatment of reaction mixture freshly prepared magnesium hydroxide suspension, silica sol, lithium fluoride solution. The starting Mg(OH)₂ : SiO₂ : LiF molar ratio was 1 : 1.51 : 0.25. Hybrid systems have been synthesized by heat treatment of synthetic layered magnesium silicate in water-ethanol solution of chlorin e₆ 13 (1), 17(3)-N,N'-(2-hydroxyethyl) diamide 15(2)-methyl ester. The systems contain of 0.85·10⁻⁶ and 1.4·10⁻⁶ mol of the organic component per 1 g of layered magnesium silicate. The introduction of the chlorin e₆ derivative into hectorite type layered magnesium silicate sol promotes the aggregation processes and growth particles of the hybrid samples (250±5 nm), as compared with the particles of magnesium silicate (133±1 nm). X-ray phase analysis, UV-Vis spectroscopy and laser Doppler electrophoresis studies have been allowed to establish that non-aggregated molecules of the chlorin e₆ derivative are located on the surface of magnesium silicate particles. UV-Vis spectroscopy study showed protonation of nitrogen atoms of the chlorine macrocycle of the chlorin e₆ derivative molecules (Soret band 405-406 nm; Q-band 642-643 nm) by hydroxyl groups of the layered magnesium silicate. Chlorin e₆ 13 (1), 17(3)-N,N'-(2-hydroxyethyl) diamide 15(2)-methyl ester sorption on the surface of magnesium silicate particles occurs due to electrostatic interaction between protonated chlorine e₆ derivative molecules and ionized hydroxyl groups of the magnesium silicate.

References

- [1] L.A. Tulaeva, E.A. Ryabikova, and D.V. Belykh. Synthesis and study of chlorophyll *a* diamide derivatives with an aromatic substituent at the amide nitrogen atom. *Butlerov Communications*. **2018**. Vol.54. No.6. P.19-34. DOI: 10.37952/ROI-jbc-01/18-54-6-19
- [2] E.I. Pushkareva, and D.V. Belykh Interaction of methylpheophorbide with butylamine and piperidine. *Butlerov Communications*. **2016**. Vol.48. No.12. P.38-41. DOI: 10.37952/ROI-jbc-01/16-48-12-38
- [3] S. Kwiatkowski, B. Knap, D. Przystupski, J. Saczko, E. Kędzierska, K. Knap-Czop, J. Kotlińska, O. Michel, K. Kotowski, J. Kulbacka. Photodynamic therapy – mechanisms, photosensitizers and combinations. *Biomedicine & Pharmacotherapy*. **2018**. Vol.106. P.1098-1107.
- [4] M. Urbani, M. Grätzel, M.K. Nazeeruddin, T. Torres. Meso-Substituted Porphyrins for Dye-Sensitized Solar Cells. *Chemical Reviews*. **2014**. Vol.114. No.24. P.12330-12396.
- [5] M. Eguchi, T. Shimada, H. Inoue, and S. Takagi. Kinetic Analysis by Laser Flash Photolysis of Porphyrin Molecules' Orientation Change at the Surface of Silicate Nanosheet. *J. Phys. Chem. C*. **2016**. Vol.120. No.13. P.7428-7434.
- [6] D. Tokieda, T. Tsukamoto, Y. Ishida, H. Ichihara, T. Shimada, S. Takagi. Unique fluorescence behavior of dyes on the clay minerals surface: surface fixation induced emission (S-FIE). *Journal of Photochemistry and Photobiology A: Chemistry*. **2017**. Vol.339. P.67-79.
- [7] Y.I. Pylina, I.S. Khudyaeva, E.A. Osipova, D.M. Shadrin, I.O. Velegzhaninov, E.S. Belykh, and D.V. Belykh. Synthesis, cytotoxic and genotoxic activity of new chlorine-containing chlorophyll *a* derivatives. *Butlerov Communications*. **2018**. Vol.55. No.8. P.10-15. DOI: 10.37952/ROI-jbc-01/18-55-8-10
- [8] N.A. Zherdetsky, N.U. Shlyahin, S.B. Romadenkina, and 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
- [9] E.A. Tarasenko, and O.E. Lebedeva. Ferrosilicates with low iron content in oxidation processes. *Butlerov Communications*. **2018**. Vol.55. No.9. P.86-90. DOI: 10.37952/ROI-jbc-01/18-55-9-86

- [10] Y. Ide. Efficient Photocatalytic Systems Integrated with Layered Materials Promoters. P.395-407. In: *Inorganic Nanosheets and Nanosheet-Based Materials. Nanostructure Science and Technology*. Editors: T. Nakato, J. Kawamata, S. Takagi. *Tokyo: Springer. 2017*. P.542.
- [11] D.R. Kosiur. Porphyrin adsorption by clay minerals. *Clays and Clay Minerals. 1977*. Vol.25. P.365-371.
- [12] F. Bergaya and H. Van Damme. Stability of metalloporphyrins adsorbed on clays: a comparative study. *Geochimica et Cosmochimica Acta. 1982*. Vol.46. No.3. P.349-360.
- [13] N. Kaufherr, S. Yariv, L. Heller. The effect of exchangeable cations on the sorption of chlorophyllin by montmorillonite. *Clays and Clay Minerals. 1971*. Vol.19. P.193-200.
- [14] Y. Kodera, H. Kageyama, H. Sekine, Y. Inada. Photo-stable chlorophylls conjugated with montmorillonite. *Biotechnology Letters. 1992*. Vol.14. No.2. P.119-122.
- [15] A. Ish, T. Itoh, Y. Kodera, A. Matsushima, M. Hiroto, H. Nishimura, Y. Inada. Photostable Chlorophyll a - Bentonite Conjugate Exhibits High Photosensitive Activity. *Research on Chemical Intermediates. 1997*. Vol.23. No.8. P.683-689.
- [16] J. Xiong, C. Hang, J. Gao, Y. Guo, C. Gu. A novel biomimetic catalyst templated by montmorillonite clay for degradation of 2,4,6-trichlorophenol. *Chemical Engineering Journal. 2014*. Vol.254. P.276-282.
- [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. No.1. P.77-82.
- [18] I.V. Loukhina, O.M. Startseva, A.Yu. Bugaeva, B.N. Dudkin, D.V. Belykh. Modification of Magnesium Silicate with 13(1)-N-Methylamide-17-methyl-15-diethylene Glycol Ester of Chlorin e₆. *Russian Journal of General Chemistry. 2016*. Vol.86. No.8. P.1805-1810. (russian)
- [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 e₆. *Russian Journal of General Chemistry. 2017*. Vol.87. No.5. P.912-917. (russian)
- [20] Z. Chernia, D. Gill. Flattening of TMPyP Adsorbed on Laponite. Evidence in Observed and Calculated UV-vis Spectra. *Langmuir. 1999*. Vol.15. No.5. P. 1625-1633.
- [21] S. Takagi, T. Shimada, M. Eguchi, T. Yui, H. Yoshida, D.A. Tryk, H. Inoue. High-Density Adsorption of Cationic Porphyrins on Clay Layer Surfaces without Aggregation: The Size-Matching Effect. *Langmuir. 2002*. Vol.18. No.6. P.2265-2272.
- [22] 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. DOI:10.1016/j.solener.2004.03.029.
- [23] D.V. Belykh, L.P. Karmanova, L.V. Spirikhin, and A.V. Kuchin. Synthesis of amide derivatives of chlorin e₆. *Russian Journal of Organic Chemistry. 2007*. Vol.43. No.1. P.126-134. (russian)
- [24] N.G. Klyuchnikov Workshop on inorganic synthesis. *Moscow: Enlightenment. 1979*. 270p. (russian)
- [25] M. Reinholdt, J. Miehé-Brendle, L. Delmotte, M.-H. Tuilier, R. le Dred, R. Cortes, and A.-M. Flank. Fluorine Route Synthesis of Montmorillonites Containing Mg or Zn and Characterization by XRD, Thermal Analysis, MAS NMR, and EXAFS Spectroscopy. *Eur. J. Inorg. Chem. 2001*. P.2831-2841.
- [26] K.A. Carrado. Synthetic organo- and polymer-clays: preparation, characterization, and materials applications. *Applied Clay Science. 2000*. Vol.17. No.1. P.1-23.
- [27] M. Reinholdt, J. Miehé-Brendlé, L. Delmotte, R. Le Dred, M.-H. Tuilier. Synthesis and characterization of montmorillonite-type phyllosilicates in a fluoride medium. *Clay Minerals. 2005*. Vol.40. No.2. P.177-190.
- [28] 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.
- [29] R.E. Grim. *Clay Mineralogy. New York: McGraw-Hill. 1953*. 384p.
- [30] S.S. Cady, T.J. Pinnavaia. Porphyrin intercalation in mica-type silicates. *Inorganic Chemistry. 1978*. Vol.7. No.6. P.1501-1507.
- [31] 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.