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Orientation and optical properties of methylene blue crystal for better understanding of interactions with clay mineral surface

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The properties of cationic dye Methylene blue (MB) adsorbed on diferent surfaces have been investigated intensively over the years and various models for the orientation of its cations have been proposed (Hang and Brindley, 1970; Bujdak et al., 2003; Li and Zare, 2004; Marr III et al., 1973; Bujdak, 2006).The main objective of this work is to investigate and determine orientation and optical properties of metylene blue crystal upon its crystallization on a glass slate and to use those findings in better understanding of interactions with clay minerals. Cationic dyes have very high affinity for clay surfaces and those interactions are easily detected, therefore these dyes are used to determine several properties of clay surfaces (morphology, layer charge, CEC).
For this study, we have selected a group of MB crystal and carried out XRD analysis, polarized absorption spectra measurement (400 – 900 nm) and determination of optical properties (pleochroism, determination of twining and extinction angle) using polarizing microscope.
Methylene blue crystals are exhibiting mostly needle like habitus with huge difference in width – length ratio. According to X-ray diffraction it is quite obvious that the y (b) axis is perpendicular to the crystal surface. The x (a) and z (c) axis lie in the crystal plane (010). Crystals exhibit prominent dichroism: from blue (E ∥ elong.) to colorless. In accordance with current interpretation of MB spectra peaks at 647 and 570 nm can be assigned as dimer aggregation and peaks at 475 and 406 nm as higher level of aggregation. All of them exhibit pronounced polarization dependence. The group of peaks at lower energy (700 to 900 nm) do not show significant polarization dependence and they correspond to the J - aggregates. Peak at around 800 nm have been noticed as fluorescence active. In dependence with thickness of the crystals and vibration direction we have observed presence of polysynthetic twinning which can be compared with polysynthetic twinning of feldspar minerals.
Final result of molecular polymerization is represented as crystal framework of methylene blue. Model of the MB molecular aggregation in the crystal structure could be used as a way for the interpretation of the thin layer structure and the molecular aggregation on the clay surface.

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