

## MOLECULAR SIMULATIONS OF MONTMORILLONITE INTERCALATED WITH RHODAMINE B: INTERLAYER AND SURFACE STRUCTURE AND FLUORESCENCE PROPERTIES

POSPÍŠIL, M.,<sup>1</sup> ČAPKOVÁ, P.,<sup>1</sup> MALÝ, P.,<sup>1</sup> WEISSMANNOVÁ, H.,<sup>2</sup> KLIKA, Z.,<sup>2</sup> VALÁŠKOVÁ, M.,<sup>2</sup> WEISS, Z.<sup>2</sup>

<sup>1</sup> Department of Chemical Physics and Optics, Charles University [Katedra chemické fyziky a optiky, Univerzita Karlova], Ke Karlovu 3, Praha, 121 16, Czech Republic

<sup>2</sup> Institute of Materials Chemistry, Technical University of Ostrava [Vysokoškolský ústav chemie materiálů Technická univerzita Ostrava], tř. 17. listopadu 15, Ostrava–Poruba, 708 33, Czech Republic

E-mail: Pospisil@karlov.mff.cuni.cz

Silicates, especially montmorillonites attract attention in wide field of industrial research due to their specific properties. One way of possible montmorillonite modification lies in branch of intercalation processes. Intercalation can be based either on ion exchange (original ion exchange cations are replaced by organic cations) or ion dipole interaction (ion exchange cations remain and organic species are intercalated into interlayer space). Intercalation of optical active species is special and very interesting area because of silicate layers are transparent in visible spectra. The optical active cations (rhodamine B) were intercalated into interlayer space (Pospíšil et al., 2003) and also were remained on the surface of silicate layers. So, the knowledge of structure properties relationship is crucial for describing optical properties of these intercalated samples.

Structure analysis showed that the interlayer and the surface structures are very different in arrangement of rhodamine B cations with respect to silicate layers. Moreover the structure arrangement strongly depends on the guest concentration in the intercalation solution and on the way of sample preparation. The increasing of rhodamine B concentration change arrangement of guest in relative proportions of monomers, dimmers and higher aggregates adsorbed on the external surface and intercalated into the interlayer space. These changes in rhodamine B arrangement can be observed by experimental methods such as X-ray diffraction and fluorescence. For correlation of structure and fluorescence changes molecular mechanics and classical molecular dynamics were used. Molecular simulations were carried out in Cerius<sup>2</sup> modelling environment.

Combination of theoretical and experimental methods show: a) the surface and interlayer structure for given sample is different and b) the concentration dependence of rhodamine B cations arrangement is different for the surface and interlayer structure. The most important difference between surface and interlayer structure occurs in case of fully exchanged samples i.e. between the models with four rhodamine B cations per one  $3a \times 2b \times 1c$  supercell in the interlayer space of montmorillonite and four rhodamine B cations per one  $6a \times 2b$  surface supercell of montmorillonite. In the interlayer space the most stable structure with the highest sublimation energy (calculated by molecular mechanics method) is the bilayer arrangement of rhodamine B cations with xanthenes parallel with the silicate layers. However on the fully exchanged sample surface the most stable structure is the J-dimeric arrangement with xanthene planes tilted to the surface of silicate layer.

Fluorescence measurements of the samples show that increasing loading of rhodamine B cations leads to the red shift of the fluorescence band. However the fluorescence band shape exhibits more complicated behaviour in dependence on concentration. The irregularity in the concentration dependence of these spectral characteristics can be described as a result of joint action of surface and interlayer arrangement of rhodamine B cations in montmorillonite structure.

### Reference

POSPÍŠIL, M. et al. (2003): Journal of Molecular Modelling, **9**, 39–46.