

CHARACTERISATION OF THE LAYER CHARGE OF REDUCED-CHARGE MONTMORILLONITES

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A series of reduced-charge montmorillonites (RCMs) was prepared from SAz-1 montmorillonite (Arizona) saturated with Li^+ cations. Portions of the Li^+ -saturated montmorillonite were heated at various temperatures (60–200°C) for 24 hours. The extents of the charge reduction were proportional to the preparation temperature. Series of RCMs provides a good model for studying the effects of the layer charge on properties of smectites. The layer charge of prepared samples was characterised by cation exchange capacities (CECs), layer charge density measurements using alkylammonium method and by means of spectra of organic, cationic dyes in clay dispersions.

The CEC values were measured and compared using several methods. These methods were based on ion exchange reactions with ammonium acetate, barium chloride, methylene blue (MB) and copper complex of triethylenetetramine. The values of CEC decreased with preparation temperature. There were non-significant differences between the CEC values determined by different methods. Only in the case of methylene blue adsorption, slightly higher values were observed due to MB adsorption above CEC.

The layer charge of the RCMs was measured using alkylammonium method. In comparison with the CEC values, this method gave information about the charge densities in the interlayer space of the minerals. Layer charge distribution histograms and average charge densities were calculated. The

charge distributions of parent and all prepared RCMs are heterogeneous. The mean values of charge densities were used for the calculation of theoretical CECs.

The interactions of the prepared materials with two cationic dyes, methylene blue (MB) and thionine (Th) were studied in detail. Spectral properties of dye cations adsorbed at the silicate surface reflected significantly the charge density of the prepared materials. The distribution of the layer charge probably controlled the distances between adsorbed dye cations. The surfaces of high charge densities promoted and those of low charge densities suppressed the dye cation aggregation. The parent material with the highest charge density induced the formation of H-aggregates of the dye cations with sandwich-type molecular assemblies. The H-aggregates absorb light at significantly lower wavelengths with respect to monomers. The amount and the size of the H-aggregates decreased with decreasing layer charge in favour of H-dimers and monomers.

Comparisons of the spectral properties of adsorbed MB and thionine (Th) were investigated as well. The trends of the Th aggregation were similar to those of MB. Differences between MB and Th spectra were observed in the presence of high charge RCMs. Th exhibited a tendency to react on the surfaces of high charge silicates. This reaction is probably similar to those observed with other aromatic amines adsorbed on the clay mineral surfaces.