

ADSORPTION AND AGGREGATION OF A CATIONIC CYANINE DYE ON LAYERED SILICATES

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Layered inorganic materials are suitable starting materials to build up highly organized inorganic-organic nanostructures utilizing their two dimensional surfaces. By introducing photoactive species on such materials, important information on the distribution and location of guest species can be obtained from spectroscopic measurements. Resulting nanocomposites may be applicable as photofunctional materials. 1) In this study, we report the adsorption and aggregation of a cationic cyanine dye, 1,1'-diethyl-2,2'-cyanine (pseudoisocyanine, PIC), on clay minerals and a layered polysilicate, a synthetic Na-magadiite. PIC forms a specific aggregate, so called J-aggregate, and the spectral features reflect the state of the PIC. Since J-aggregates of cyanine dyes exhibit useful optical properties, fixation of cyanine dye on layered materials is worth investigating. The adsorbed PIC formed J-aggregates on Na-montmorillonite (Kunipia F from Kunimine Industries Co.) and synthetic Na-fluor-tetrasilic mica (from Topy Industries Co.), while they distributed molecularly on synthetic Na-saponite (Sumecton SA from Kunimine Industries Co.) and synthetic Na-hectorites (SWN from Coop Chemical Co. and Laponite RD from Laponite Industries Co.). The particle size of the clays was considered to be a dominant factor to control the aggregation of PIC. The use of magadiite instead of clays and coadsorption of photoinactive species were also found to be effective ways to control the state of the PIC.

References

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NEW DEVELOPMENTS IN ORGANOCLOYS

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Since their development at the Mellon Institute in the 1940's, the organocloys, particularly the organobentonites, have been materials of commerce. Traditional manufacturing techniques involve centrifugal separation of sodium smectites followed by treatment in the aqueous phase with quaternary amine salts. The resulting product consist of both the silicate sheet and organic cations in crystallographically identifiable positions. This structure imparts unique properties in a solvent system containing organobentonites. Consequently, these products enjoy use primarily as rheological control agents in solvent systems. Initially, these materials required use of a polar additive to attain maximum viscosity. Several strategies now employed can minimize or avoid the need for these additives. Although vigorous development has allowed conventional organobentonites to maintain markets, conversion of many applications from solvent to water based formulations limits growth. Consequently, organobentonites useable in water systems have appeal. Conventional treatment with highly hydroxylated organic compounds, neutral or cationic, can impart some of the desirable properties. A new technique combining biphasic separation with simultaneous surface treatment shows promise. The technique can remove non-smectite mineral phases without need for the sometimes troublesome centrifugation step. The smectite can then react with hydroxylated organic compounds to form a product dispersible in water. This product has attractive properties for controlling rheology in many industrial applications.

EVALUATION OF CLAY BEHAVIOR IN ACID SULFATE ENVIRONMENT USING THE TEST-MINERAL METHOD

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The test-mineral technique is widely employed in field as a mean of

assessing the chemical soil processes. Na-saturated vermiculite was used as a reference mineral and placed in ion-permeable polyamide bags that were buried in clayey acid sulfate soils belonging to three main environments of Lower Casamance (Senegal): (i) highly saline soil, daily waterlogged by concentrated seawater (Koubalan site, Kb), (ii) weakly saline soil, seasonally flooded by severely acid runoff water stored in a small reservoir (Djiguinou site, Dj); (iii) weakly saline soil, seasonally flooded by acid ground water uptake (Katoure site, Ka). Bags were recovered from each soil after one year and analyzed for exchangeable cations, cation-exchange capacity (CEC), extractable Al and Fe, and X-ray diffractometry (XRD) before and after treatments with KCl, Na citrate, ammonium oxalate and dithionite-citrate reagents. In Dj soil, exchangeable Na on the vermiculite was mainly replaced with Al and CEC approximately decreased by 90%. Large amounts of free Al were extracted by Na citrate reagent leading to the formation of a hydroxylated interlayer Al which was confirmed by XRD analysis. In Ko soil vermiculite was weakly affected, Ca having partly replaced Na. Vermiculite from Kt soil lost 25% of its CEC, exchangeable Na being displaced by Ca. The vermiculite proved to be an excellent indicator of the chemical environment of acid sulfate soils, giving new arguments for modelling the formation of Al and Fe rich sulfates in dry conditions.

CATION EXCHANGE, WATER UPTAKE, AND SWELLING PRESSURE OF MX-80 IN CONTACT WITH BRINE SOLUTIONS

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Cation exchange equilibria, water uptake and swelling pressure of MX-80 bentonite were determined with two sets of saline solutions. The first set of eleven solutions exhibits a constant normality of 5,9N, with varying concentration ratio of Mg and Na, and constant concentrations of Ca and K. The second set consists of five geochemically relevant solutions, each of which are NaCl-saturated and in equilibrium with a different set of mineral phases encountered in underground salt rock formations (NaCl-solution, IP9, IP19, IP21, IP22, IP24). Chemical analysis indicates a substantial adsorption of univalent chlorocomplexes of the type MCl^+ ($M=Mg, Ca$). Cation exchange with the first set of solutions can be modelled using a selectivity coefficient, which implies solution phase and sorbed phase concentrations and effective valency of Mg and Ca in solution. Interlayer spacing and total water content were investigated in compacted samples, equilibrated with any of the solutions. Both parameters are positively correlated with the Mg/Na-ratio in solution. So far on the basis of the data it is not possible to distinguish reliably quantitatively between interlayerwater and porewater. The Mg content in solution correlates with the interlayer water and also with the swelling pressure. The swelling pressure experiments demonstrate that MX-80 acts as a semipermeable membrane, which renders the reacting solution to a much lower salinity in an intermediate state. With a Mg-rich solution this even leads to a higher transient swelling pressure than at the end of the experiment.

THE REGULARITIES OF THE STRUCTURE-FORMATION OF ALKYLAMMONIUM MONTMORILLONITES (AM) IN ORGANIC MEDIA

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This work gives the results of the rheological, X-ray diffraction, electrokinetic and thermodynamic investigations of the AM-organic liquid system. It allowed us to establish and explain the following regularities of the AM gel-formation in the organic media of different polarity:

1. The necessary but deficient condition for the effective AM gel-formation is their ability for intracrystalline swelling and dispersing in the given medium. The swelling degree and the possibility of spontaneous dispersing are determined by the ratio between the energy of the AM structural layer bond and the solvation energy, with the account of the entropic effect.
2. The AM thickening ability is the extremal function of the modification degree, more exactly, the surface lyophilization.
3. The linear increase of the rheological parameters of the AM organogels in the order benzene - toluene - p-xylene - o-xylene -

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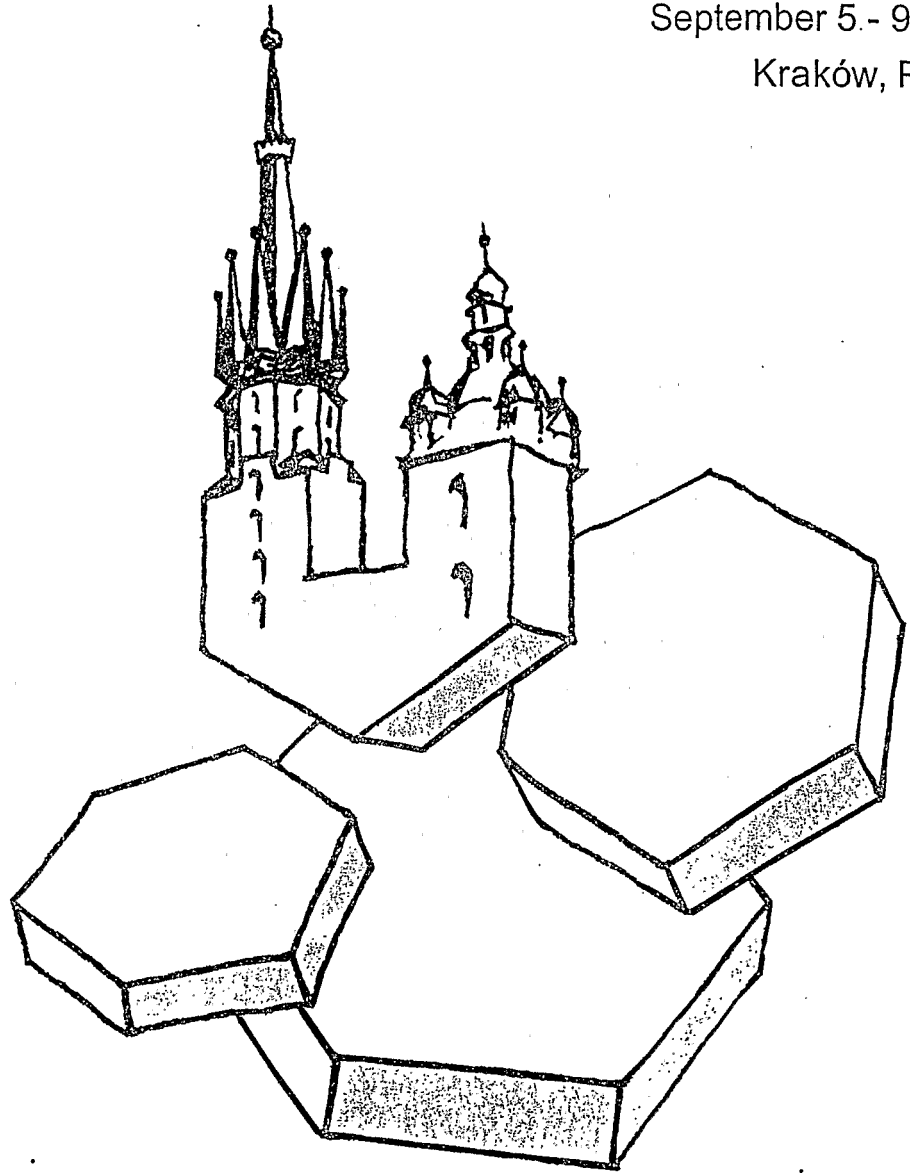


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