Influence of Organic and Inorganic Salts on the Coagulation of Montmorillonite Dispersions

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Abstracts: The colloidal state (stable, coagulated, or gel-like) and the rheological properties of Na-rich montmorillonite (Wyoming) dispersions are strongly influenced by organic cations. This effect is shown for homologous organic cations: alkyl trimethylammonium ions, paraquat, diquat, alkyl bispyridinium ions, and the triphenylmethane dyes crystal violet, methyl green, and tris (tri-methylammonium phenyl) methane chloride. The critical coagulation concentrations, c_κ, are small (often < 1 mmol/L) because the cations are enriched in the Stern layer and influence the solvent structure near the surface. The strong adsorption of the counterions at the clay-mineral surface causes c_κ values to increase with the solid content. Charge reversal (recharging) of the particles was observed with the longer chain alkyl trimethyl-ammonium ions, dodecyl bispyridinium ions, and crystal violet. Other cations reduced the electrophoretic mobility to zero but positive particle charges were not observed.

The plastic viscosity increased sharply at the critical coagulation concentration and showed a minimum slightly below c_κ, which was caused by the electroviscous effect. Yield values were developed at concentrations above c_κ. In most cases, yield values reached a plateau where the amount of organic cations was ~0.5 mmol/g, *i.e.*, about half of the cation-exchange capacity. The c_κ values decreased with increasing hydrophobicity of homologous compounds, but the yield value showed maxima at intermediate chain lengths. The yield value of several 0.5% dispersions was high, *e.g.*, dodecyl trimethylammonium ions, 71 Pa; paraquat, 100 Pa; diquat, 42 Pa; hexyl bispyridinium ions, 53 Pa (*vs.* Ca^{2+}, 0.2 Pa; Al^{3+}, 0.7 Pa). The storage modulus as a function of the number of organic cations changed in a similar way as the yield value, and high values were observed (*e.g.*, dodecyl trimethylammonium ions, hexyl bispyridinium ions: 1000 Pa, paraquat: >4000 Pa). Thus, dispersions with high viscosity, yield value, and pronounced viscoelasticity are obtained by coagulating Na-rich montmorillonite dispersions with organic cations.

Key Words: Alkyl Bispyridinium Ions • Alkyl Trimethylammonium Ions • Critical Coagulation Concentration • Colloids • Crystal Violet • Diquat • Flocculation • Methyl Green • Montmorillonite • Paraquat • Rheology • Viscoelasticity

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