Electrostatic interactions in charged colloidal clay suspensions

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Natural swelling clay minerals are negatively charged platelets whose charge is compensated by exchangeable cations. Homoionized by monovalent cations, they form gels at low volume fractions \(\phi\) which are widely used in industrial and health applications. Since the pioneering works of Freundlich and Langmuir [1-2], the structure of such gels and the mechanisms of gelation have been debated with two conflicting views: (i) a tridimensional (“house of card”) network of the gel based on electrostatic attraction between the edges and faces of the platelets or (ii) the stabilization of the gel structure by a repulsive process between the interacting electrical double layers of the platelets. We have recently shown that tetrahedrally substituted clays exhibit an isotropic-to-nematic phase transition at lower concentration than that of the sol-gel transition [3-5] while in most of the swelling clays studied so far, the I/N transition seems to be hindered by the sol-gel transition.

For studying this problem, we have chosen to work with size-selected natural swelling clays, one beidellite and three montmorillonites. Osmotic stress experiments were performed to obtain a wide concentration range of clay suspensions varying from the liquid to the gel phase. All samples were further analyzed by combining TEM observations and Small Angle X-Ray Scattering (SAXS) experiments. The swelling laws (correlation distance vs volume fraction) obtained from SAXS experiments display a crossover from isotropic volumic swelling \((\phi^{-1/3})\) close to the sol-gel transition to local lamellar order \((\phi^{-1})\). Furthermore, the average thickness of the individual objects derived from the swelling laws is close to that of a single clay sheet (0.65 nm). Combined with the morphological parameters derived from TEM, the swelling laws can be at the first-order well approached on the basis of excluded volume interactions. Finally, osmotic pressure measurements reveal that the system can be approached from a simple Poisson-Boltzmann treatment revealing that for ionic strength below \(10^{-3}\) M/L, clay suspensions are purely repulsive while a discrepancy occurs between tetrahedrally and octahedrally substituted clays over two orders of magnitude.