

ELASTIC NETWORK OF LAMELLAR PARTICLES: FORMATION AND RHEOLOGICAL CHARACTERISATION

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In aqueous systems, the colloidal interactions between clay mineral particles are generally governed by local electrostatic field developing around particles due to the neutralisation of surface charges. The composition of aqueous solution influences both the surface charging and the charge neutralisation. Among clay minerals montmorillonite (2:1 layer silicate) as the most often studied swelling clay was chosen for a comprehensive study to show how the pH dependent surface charge heterogeneity of clay lamellae influences the particle interactions in suspensions and the structure of particle network formed in montmorillonite gels. The layers of montmorillonite lamellae have permanent negative charges due to isomorphic substitutions, and pH-dependent charges develop on the surface hydroxyls at the edges. Wyoming montmorillonite sample (SWy-2) was studied. Specific patch-wise charge heterogeneity of montmorillonite lamellae, i.e. oppositely charged surface parts of layers, exists only under acidic conditions. Edge-to-face heterocoagulated structure forms below pH of PZC of edges ($\text{pH}_{\text{PZC,edge}} \approx 6.5$) and above a threshold salt concentration, where the hidden electric double layer of positively charged edge region has emerged.

In any colloidally stable suspensions the overall particle interaction is repulsive, while more or less loose physical network of adhered particles forms in the unstable suspensions. Whatever the reason, the formation of particle networks strongly affects the mechanical, flow properties of clay suspensions. In general, stable suspensions show liquid-like (viscous) Newtonian flow behaviour with shear thinning or thickening character, while the appearance of plastic character frequently together with thixotropy refers to the network formation of aggregated particles. The rheology of clay suspensions is the subject of tremendous works for several decades, especially because of the wide-ranging practical application. It was supposed that the solid-like gels formed spontaneously from the thin lamellae due to Coulombic attraction between oppositely charged parts of montmorillonite plates have elastic character within a limited range of applied stress, which is presumably comparable with the characteristic yield values of particle networks.

Characteristic changes in gel formation and in rheological properties induced by decreasing pH in dense suspensions containing 0.01 M NaCl provided experimental evidence for the structure of particle network. Static and dynamic methods were used to study the viscoelastic properties of montmoril-

lonite gels. Several series of creep tests and forced oscillation measurements were performed. A significant increase in thixotropy and yield values, and also the formation of viscoelastic gels below $\text{pH} \approx 6.5$ verify that attractive interaction exists between oppositely charged parts of lamellar particles in the less concentrated systems. However, solid-like feature with pronounced viscoelasticity, more or less strong network of lamellar particles with large yield values can form in more concentrated montmorillonite suspensions even at higher pHs. It can be stated that different types of elastic network can form from montmorillonite lamellae depending on the pH of aqueous medium containing 0.01 M indifferent electrolyte: a) strong attractive gel with significant elasticity forms in acidic suspensions below the pH of edge PZC (cca. 6.5) due to the electrostatic attraction of oppositely charged edges and faces, b) the formation of attractive gel is probable in neutral suspensions, where no electrostatic attraction exists between neutral edges and negative faces, however, the random collision of lamellae results in edge-to-face particle network with definite elasticity, c) less elastic repulsive gel with rather liquid-like behaviour can form above the pH of edge PZC under alkaline conditions, because the negatively charged edges repel the negative faces of plates, only in more concentrated suspensions. The elastic response of viscoelastic montmorillonite gels is significant, if the applied stress is below or at their yield values, however, above that limits viscous character of suspensions becomes dominant.

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