

SURFACE CHARGE HETEROGENEITY EXPRESSION IN AGGREGATION OF MONTMORILLONITE LAMELLAE

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Montmorillonite layers have permanent negative charges due to isomorphous substitutions, and pH-dependent charges develop on the surface hydroxyls (Si-OH, Al-OH) at edges. Acid-base titration of well defined Na-montmorillonite suspension at different ionic strengths has been proved to be acceptable to characterise the pH-dependent charge development on amphoteric edge sites and to determine the point of zero charge (PZC) of edges. The evaluation of reversible net proton surface excess vs. pH functions has revealed that the OH groups at edges having PZC at $\text{pH} \approx 6.5$ are less basic than the Al-OH sites of alumina and less acidic than the Si-OH groups on silica surface. Positive charges can develop in a protonation reaction of Al-OH sites at edges only at pHs below cca. 6.5, and deprotonation of Si-OH, then that of the Al-OH sites takes place with increasing pH of solution resulting in negative charges at edges. Therefore, the patch-wise charge heterogeneity of montmorillonite, i.e. oppositely charged surface parts of platelets, exists only under acidic conditions, which may remain hidden at low salt content due to the spillover of the negative electrostatic field emanating from the face of montmorillonite plates. The effect of pH and indifferent electrolytes is mutual; none of them can be interpreted alone.

Coagulation kinetics measurements resulted in reliable stability ratio data for fine montmorillonite sols at different pHs, and provided indisputable characterisation of hetero- and homo-coagulation. Edge-to-face hetero-coagulation occurs above NaCl concentration 25–26 mmol/l at $\text{pH} \approx 4$, where the hidden electric double layer (EDL) of positively charged edge region has emerged. Edge-to-face attraction between the poorly charged edges and negatively charged faces of platelets around the pH of PZC of edges ($\text{pH}_{\text{PZC, edge}} \approx 6.5$) in relatively low concentration of the indifferent electrolytes (typically around 50 mmol/l NaCl) is probable. The homo-coagulation of uniformly charged lamellae at pH 8–8.5, formation of face-to-face aggregates requires much higher salt concentration (typically around 100 mmol/l NaCl) to compress the dominant edl on the highly charged faces of particles.

The surface charge heterogeneity of highly anisometric montmorillonite plates influences the ordering of lamellae in

the self-oriented films. X-ray diffraction patterns of montmorillonite films prepared from slightly acidic suspensions proved that formation of well ordered layer packages is hindered by the attraction between edges and faces. Random edge-to-face fractal aggregates form below $\text{pH} \approx 7$, while well oriented face-to-face structure can develop, if the pH of initial suspension is above $\text{pH} \approx 8$.

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. A significant increase in thixotropy and yield values, and also the formation of viscoelastic gels only at and below $\text{pH} \approx 6.5$ verify that attractive interaction exists between oppositely charged parts of lamellar particles. The lower the pH the larger the amount of positive charges on the edges of montmorillonite lamellae, therefore the attraction between the positively charged edges and negative basal plates becomes stronger with decreasing pH above the critical $\text{pH} \approx 4$ of the acidic dissolution of crystal lattice.

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