

# Adsorption and migration of oxide particles on mica/water interface

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The adsorption of colloidal particles onto a solid substrate is in general assumed as a nearly irreversible process. More precisely, one assumes that in the vicinity of a surface, the colloidal particles would have only one choice : either be depleted by the surface if the interaction is repulsive or be adsorbed and blocked at their point of adsorption when the interaction potential is attractive and the energy of adhesion very high. We have shown that a third mechanism (surface migration) can occur when surface complexing molecules are present in solution.

Aqueous dispersions of two types of oxide,  $\text{CeO}_2$  nanoparticles (7 nm in diameter) and  $\alpha\text{-Al}_2\text{O}_3$  (150 nm in diameter) have been used to adsorb layers of particles onto freshly cleaved mica sheets. Our initial goal was to control the adhesion of particles onto the substrate through the complexation of their surface with organic molecules (citric acid and acetylacetone).

An Atomic Force Microscope (AFM) was used to characterize the morphology of the layers after adsorption and a Surface Force Apparatus (SFA) and modified AFM (*m*AFM) were used to measure directly the forces acting between  $\text{CeO}_2$  or  $\text{Al}_2\text{O}_3$  particles and mica.

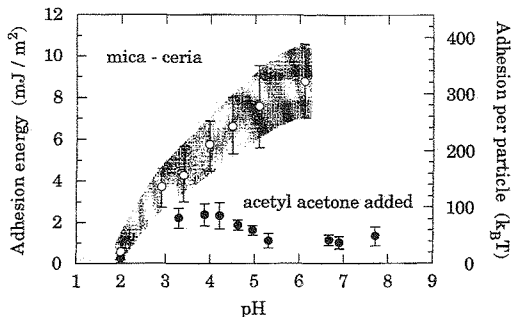


FIG. 1. Adhesion between ceria particles and mica versus pH (in absence and in presence of surface complexing molecules).

## Irreversible adsorption

In the case of ceria particles, a submonolayer with a maximum density of 22% was built spontaneously onto the mica. The adsorption was totally irreversible even for very long times of incubation in free particles water. This is due to a very high energy of adhesion of the particles onto mica as soon as the pH gets above 3 (Fig. 1) [1]. The addition of an organic molecule (acetylacetone) has a weak effect on the energy of adhesion which remains high.

## Migration of alumina particles onto mica in presence of citrates

In the case of alumina, the situation is more complex. When the particles are positive, they spontaneously form an irreversibly adsorbed submonolayer on the negative mica and the repulsions between the particles control the density of the layer. An addition of salt in the initial dispersion decreases the range of the repulsions between particles and yields to a denser submonolayer. When the sign of the particles is inverted before adsorption by complexing their surfaces with citrate molecules, the adsorption is prevented. These results are in agreement with the two well known mechanisms of interaction. On the other hand, when one incubates a mica sheet coated with a submonolayer of positive alumina in a dilute solution of sodium citrate, a surface migration phenomenon is observed. The surface charge of the particles has been inverted (through the complexation by citrate) and their energy of adhesion has been lowered as demonstrated by *m*AFM measurement. Further, as the citrates molecules separates slightly the particles from mica, they act as a molecular bumpers lubricating the contact between the particles and the surfaces. This situation is favourable for lateral displacements of the particles along the surface without any desorption. This two dimensional migration results in the formation of

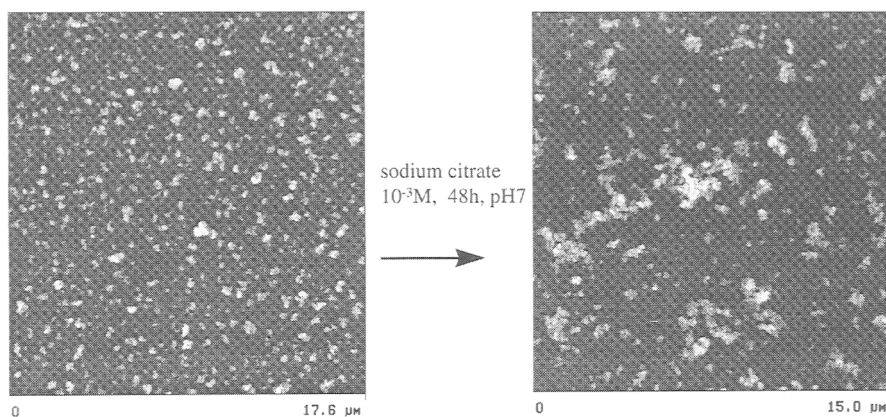


FIG. 2. AFM images of submonolayer of alumina particles (150 nm) adsorbed on mica. After 48 h of soaking in a  $10^{-3}$  M citrate solution, the particles have migrated along the surface to form two dimensional aggregates.

two dimensionnal aggregates (Fig. 2). The range of citrate concentration for which this mechanism is observed is quite small ( $10^{-4}$ – $10^{-3}$  M) and depends on pH. For higher concentration of citrates, the energy of adhesion become zero as demonstrated by *m*AFM measurement. Accordingly, the preadsorbed

layer is totally desorbed.

#### References

Spalla, O. and Kékicheff, P. (1997) *J. Coll. Interf. Sci.*, **192**, 43–65.