Phase diagram of dispersion of anisotropic particles

Abstract We discuss the phase diagram of aqueous dispersions of colloidal plate-like charged particles (300 Å × 10 Å). Particle concentration and ionic strength are the two parameters controlling the system. At fixed ionic strength, the suspensions undergo a sol/gel transition without macroscopic phase separation. Shear rheology is used to monitor this transition and to locate the appearance of the “mechanical gel” phase. Below a critical salt concentration at which flocculation appears, the transition line separating the liquid phase and the solid-like system shifts to lower volume fractions as the ionic strength increases. Direct inspection of this gel phase by cryofracture, MET and SAXS experiments shows correlated but well-separated particle populations. In order to check reversibility and equilibrium properties of this transition, the osmotic pressure was determined by an osmotic stress method. At fixed ionic strength, the osmotic pressure first increases at low particle concentration, then reaches a “pseudo plateau,” and increases again for higher concentrations. The location of such a break in the equation of state of the suspension defines a thermodynamical transition line coinciding with the mechanical phase transition. In order to analyze the origin of this gel or glassy phase, the role of particle anisotropy, coupled with diffuse layer repulsion, will be discussed.

Key words Complex fluid – sol/gel transition – colloid stability – clay suspension

Introduction

Colloidal systems undergo phase transitions such as liquid-solid [1–3], order-disorder, sol-gel [4] or glass transitions [5], which are of important technical and scientific interest. The phase diagram of the colloidal suspensions is generally controlled by interparticle interactions. While temperature and ionic strength are two intensive variables able to modulate these interactions, the morphology of the particles and their anisotropy are more subtle parameters also playing a crucial role in colloidal stability and phase transitions [6, 7].

Disk-like particle such as (Na⁺ or Li⁺ homoionic swelling clays [8–9]) are well known to form a gel above a specific volume fraction. However, the addition of salt does not promote the liquid phase, as observed for spherical or rodlike particles, but lowers the particle volume fraction at which the gel or glassy phase appears [8, 9]. At first glance, this result seems to be contrary to what one
would expect from DLVO theory. Two opposite explanations are proposed in the literature:

i) a micro flocculation due to electrostatic or van der Waals attractions between edges and faces of the plate-like particles resulting in a linked structure, the so-called house of cards configuration [10];

ii) a gelation mechanism, originally suggested by Norrish [11] and supported by others [12–14], which stresses the role of long-range electrostatic repulsion between overlapping double layers, as revealed by osmotic pressure measurements, coupled with excluded volume interactions induced by the specific anisotropy of the charged disklike particles.

The choice between attractive and repulsive interparticle interactions during gelation of disk-like particles is not easy, and the aim of this work is to provide experimental information on the phase diagram of plate-like charged particles. More specifically, we will focus on suspensions of small (300 Å x 10 Å) synthetic clay particles (laponite). This system has already been analyzed by different authors, and especially by Ramsay [13–15] and Morvan [16]. In the present work, particle concentration and ionic strength will be the two parameters controlling the system. Shear rheology will be used to monitor the sol/gel transition and to locate the appearance of the “mechanical gel” phase. Self-organization of the gel phase will be evidenced by cryofracture, MET and SAXS measurements. Finally, the reversibility and the equation of state of this colloidal system under gelation will be investigated by an osmotic stress method.

### Experimental results

#### Rheological behavior

As already shown by different authors, colloidal suspensions of laponite undergo a gel transition above some solid fraction \( C_0 \). Below this value, the suspension is slightly viscous and the elastic \( G'(\omega) \) and loss modulus \( G''(\omega) \) are weak (around \( 10^{-1} \) Pa). Above \( C_0 \), the elastic modulus increases markedly and the appearance of a yield stress is observed. \( G'(\omega) \) and \( G''(\omega) \) do not show a strong variation with frequency in the dynamical range between \( 10^{-2} \) and \( 10^{+2} \) rad/s. At fixed particle concentration, the elasticity and, incidentally, the yield stress, increase with the ionic strength. Experimental data fit a power law given by:

\[
G'(0) = (C - C_0)^\alpha \quad \text{(eq 1)}
\]

Such a power law was already observed for colloidal suspensions of clays [8, 13]. The exponent \( \alpha \) (2.35) is not sensitive to the ionic strength and the numerical determination of \( C_0 \) permits an estimation of the concentration at which gelation appears, in good agreement with the appearance of a yield stress. The resulting transition line separates a viscous sol phase from a mechanical viscoelastic gel phase. As the ionic strength increases, the clay concentration threshold is shifted towards lower values, until flocculation occurs (at \( I \approx 2 \cdot 10^{-2} \) M for NaCl).

#### Osmotic pressure and equation of state

The repulsive nature of the interparticle interaction should be confirmed by the determination of the equation of state of the suspension. The experimental results are obtained by osmotic stress of diluted laponite suspensions against Dextran solutions of fixed ionic strength at pH 10. Several remarks can be made from these results:

- the existence of a net repulsion between the laponite particles, even in the concentrated regime above the sol/gel transition;
- the salt effect agrees with the predictions of the classical DLVO theory: adding salt reduces the screening length and thus reduces the swelling pressure [17–19];
- the appearance along the different curves of a break followed by a pseudo-plateau separating the liquid and the gel phase;
- a good reversibility of the stressed suspensions which can be reswollen to give back the original sol;
- no observation of a macroscopic phase separation along the pseudo-plateau.

While the two first observations are characteristic of colloidal suspensions of charged particles of any geometry [17–19], the last observations are more interesting. The location of the first break in the osmotic pressure coincides reasonably well with the sol/gel transition line. The “mechanical” sol/gel transition appears to be directly linked with an equilibrium phase transition.

#### Microstructure and particle organization

Cryofractures and TEM observations are performed on laponite suspensions at clay concentrations of 3%, for an ionic strength \( 10^{-4} \) M (pH stabilized at 10). Under these conditions, the sample is in the gel phase. No aggregation of the clay particles may be detected. Cryofractures show a homogeneous dispersion of the particles without any direct contact. The maximum size of the trace of the laponite particles is around 400 Å, in good agreement with former determinations. SAXS is another interesting way of