

## The Colloidal and Rheological Properties of Bentonite Suspensions

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## Abstract

The objective of this paper is to give an overview of the colloidal properties of clays and to describe the work performed until the present moment in the area of adsorption of non-ionic

polymers onto clay and the rheology of clay suspensions. The review is particularly focused on  $\text{Na}^+$ -montmorillonite clay of the smectite group (Bentonite), due to its high swelling capacity, the ability to adsorb significant amount of polymer on its surfaces, and the formation of a gel-like structure with yield characteristics and viscoelastic properties at relatively low clay concentrations. A significant amount of research has been performed in these areas with applicability to various fields, such as soil science and drilling fluids, where interaction of organic polymers with the clay surface and the rheological response in the presence of electrolytes under different temperature and pressure conditions are of considerable relevance. In order to understand the interaction of these compounds with the clay surface and the rheological response of the resulting suspensions, it becomes essential to understand the structure of clay minerals, the interaction of clay particles in aqueous medium, the swelling behaviour and electrokinetic properties of  $\text{Na}^+$ -montmorillonite clay. For this reason, the above topics are addressed, along with the general features of stabilisation of colloidal particles and the adsorption mechanism of non-ionic compounds on hydrophilic surfaces. A comprehensive review of the most relevant studies of the adsorption of non-ionic surfactants and polymers onto both silica and clay is presented. Finally, an overview of the rheological behaviour of concentrated suspensions and models used to describe the flow behaviour of clay suspensions is given, along with the effect of electrolytes, polymers, high pressure and high temperature on the flow behaviour of  $\text{Na}^+$ -montmorillonite suspensions.

## Introduction

Clay minerals are extensively used in a wide range of applications. They are a key component in the formulation of ceramic products, cement, drilling fluids, moulding sands, paints and paper, among others [i]. An important characteristic that clay minerals are able to provide in such applications is adequate particle dispersion, which is necessary to obtain a uniform and stable system. Under certain conditions the clay particles may become aggregated, which leads to the variation of important properties required for a particular function. In drilling fluids, for example, the flow behaviour of the system is of utmost importance due to its circulation around the wellbore [ii]. The aggregation of the clay particles under varying conditions of temperature and electrolytes leads to strong variations of the flow properties. It becomes necessary therefore to add certain additives, or polymers, to stabilise the clay particles and prevent this behaviour. In soil science, non-ionic polymers that are water soluble have been found to impart stability to natural soil aggregates. On contact with the particle these molecules tend to collapse and spread out over the clay surface, improving the physical conditions of soil [iii]. Since non-ionic polymers appear to be well suited for stabilising a clay structure, there lies a fundamental interest to comprehend the structure and flow behaviour of the clay/non-ionic polymer systems. The purpose of this review is to highlight the advances made in the area of clay rheology and in particular the rheological properties of Bentonite suspensions both in the presence and absence of nonionic polymers.

## The Colloidal Properties of Clays

### The Clay Minerals and their Structure

The inorganic fraction of soils and natural sediments consist almost entirely of silica and various silicates. Clay minerals are hydrous silicates or aluminosilicates and may be defined as those minerals which dominantly make up the colloidal fraction of soils, sediments, rocks and waters [iv]. As they occur in nature, clays consist of a heterogeneous mixture of finely divided minerals, such as quartz, feldspars, calcite, etc., but the most colloiddally active components are one or more species of clay minerals.

The structural framework of the clay minerals is basically composed of layers comprising silica and alumina sheets joined together and stacked on top of each other. Two structural units are involved in the atomic lattices of most clay minerals [i]. One unit is called the *octahedral sheet*. It consists of two sheets of closely packed oxygens and hydroxyls in which aluminum, iron or magnesium atoms are embedded in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls (Fig. 1). The second unit is built of silica tetrahedrons and is called the *tetrahedral sheet*. In each tetrahedron, a silicon atom is equidistant from four oxygen atoms, or hydroxyls if needed to balance the structure. The silica tetrahedral groups are arranged to form a hexagonal network, and is repeated indefinitely to form a sheet of composition  $\text{Si}_4\text{O}_6(\text{OH})_4$  (Fig. 1).

The analogous symmetry and dimensions in the tetrahedral and octahedral sheets allow the sharing of oxygen atoms between the sheets. In the case of the “three-layer minerals” or *smectite* clay minerals, one alumina or magnesia sheet shares oxygen atoms with two silica sheets, one on each side. The combination of an octahedral sheet and one or two tetrahedral sheets is called a *unit layer*. Most clay minerals consist of unit layers that are stacked parallel to each other. A schematic representation of the atom arrangements in a unit cell for a three-layer clay such as *montmorillonite* is shown in Fig. 1. This structure is called the Hofmann structure [v]. Within the unit layer the unit structure repeats itself in a lateral direction. This unit structure is also called a *unit cell*.

The unit layers are stacked together face-to-face to form what is known as the *crystal lattice*. The distance between the plane in one layer and the corresponding plane in the next layer is called the *basal spacing* or *c-spacing*  $d(001)$ . The sheets in the unit layer are tied together by covalent bonds, so that the unit layer is stable. The layers in the lattice layer are held together only by Van der Waals forces and secondary valences between juxtaposed atoms. Therefore, the lattice cleaves along the basal surfaces, forming tiny mica flakes.

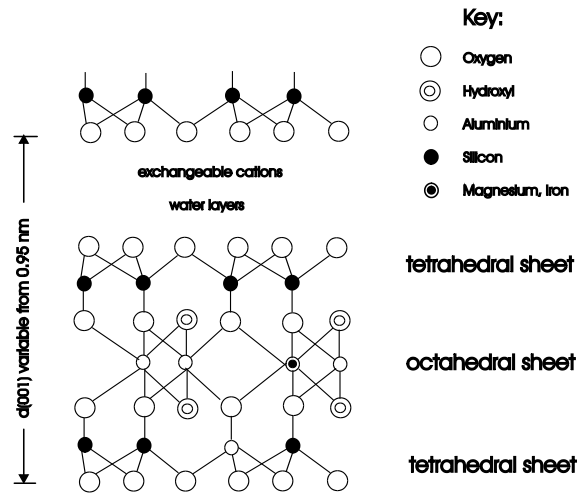


Fig. 1 The layer structure of montmorillonite according to Hofmann, Endell, Wilm, Marshall, Maegdefrau and Hendricks (Hofmann et al., [5]).

Clay mineral crystals carry a charge arising from isomorphous substitutions of certain atoms in their structure for other atoms of a different valence [vi]. In the tetrahedral sheet,  $\text{Si}^{+4}$  may be replaced by trivalent cations ( $\text{Al}^{+3}$  or  $\text{Fe}^{+3}$ ), or divalent cations ( $\text{Mg}^{+2}$  or  $\text{Fe}^{+2}$ ) may replace  $\text{Al}^{+3}$  in the octahedral sheet. When this is the case, a charge deficiency results and a negative potential at the surface of the clay is created. The negative potential is compensated by the adsorption of cations on the surface. Cations and anions are also held at the crystal edges because the interruption of the crystal along the c-axis results in broken valence bonds. In aqueous suspension, both sets of ions may exchange with ions in the bulk solution. They are known as *exchangeable cations*. The total amount of cations adsorbed on the clay, expressed in milliequivalents per hundred grams of dry clay, is called the cation exchange capacity (CEC) [vii]. It is an important characteristic of the material and a typical value for montmorillonite is one mole of univalent charge per kilogram of clay. The cation exchange capacity is high for sodium montmorillonite, comparing it to the other clay minerals [i,vii].

### Types of Clay Minerals and Montmorillonite

The most important types of clay minerals are: illites, kaolinites, attapulgites, chlorites and smectites. The first two types consist of plate-like particles that do not have an expanding lattice, therefore no water can penetrate between the layers. In illites, this is due to the strong interlayer bonding from the high layer charge, and in the case of kaolinite is due to the strong hydrogen bonding. Attapulgite particles consist of bundles of “laths”, which separate into individual laths (long shaped needles) when mixed vigorously with water. Consequently, the

rheological or flow properties of attapulgite suspensions are dependent on mechanical interference between the long laths, rather than on electrostatic interparticle forces [viii]. Chlorites differ from the above in that they possess a positive charge on one layer, balanced by an additional negative charge. Thus, normally there is no interlayer water.

The smectite 2:1 structural units are three-layer clay minerals in which one tetrahedral sheet of one unit layer is adjacent to another tetrahedral sheet of another layer. They are classified as 2:1 phyllosilicates. In this case, the oxygen atoms are opposite one another and bonding between the layers is weak. Also there is a high repulsive potential on the surface of the layers resulting from isomorphous substitution. These two last factors contribute to the increase of the c-spacing between the layers due to the penetration of water. Thus smectites have an expanding lattice, where all the layer surfaces are available for hydration and cation exchange. Interlayer surface and cation hydration between smectite structural units is a unique property of smectite clays.

Montmorillonite is the best known member of the smectite group. The montmorillonite structure is classified as *dioctahedral*, having two thirds of the octahedral sites occupied by trivalent cations. Dioctahedral montmorillonite has its structural charge originating from the substitution of  $Mg^{+2}$  for  $Al^{+3}$  in the octahedral sheet (see Figure 1). The idealised structural formula for montmorillonite is  $M_y^+ nH_2O(Al_{2y}Mg_y)Si_4O_{10}(OH)_2$  [ix]. The negative charge is balanced by cations intercalated between the structural units and these cations may be alkaline earth ions ( $Ca^{+2}$  and  $Mg^{+2}$ ) or the alkali metal  $Na^+$ . When  $Na^+$  cations are exclusively in exchange with the montmorillonite surface, the clay is known as *Na<sup>+</sup>-montmorillonite*.  $Na^+$ -montmorillonite is otherwise known as *Bentonite* (especially in drilling fluid literature). The expanding lattice may provide the clay with a specific area of as high as 800 m<sup>2</sup>/g [x]. The chemical formula for  $Na^+$ -montmorillonite is  $Na_{0.33}[(Al_{1.67}Mg_{0.33})(O(OH))_2(SiO_2)_4]$ .

### The Swelling of Montmorillonite

The swelling behaviour of clay minerals has been treated in detail by various authors [vii,xi,xii,xiii]. In this section the swelling of montmorillonite will be focused on, since it has served as a model for many years due to its high swelling capacity and its ability to form aqueous stable suspensions. In the structure of montmorillonite shown in Figure 1, only a relatively small proportion of the inorganic cations balancing the negative layer charge is located at external crystal surfaces. The majority of these cations are present in the interlayer space between the clay platelets. The thin, negatively charged sheets are held together by the electrostatic forces between alternate layers of bridging cations (typically  $Na^+$ ). When dry montmorillonite is placed in a moist atmosphere, it is able to take up water vapour by adsorbing it in the interlayer region. Swelling is the moving apart or disjoining of the clay particles, especially those in a parallel arrangement until they reach their equilibrium separation under a given pressure [xiv]. The increase in the c-spacing, or the degree of expansion of the layers planes (Fig. 2), depends on the cations located in the interlayer region, i.e. on the basal cleavage. If the interlayer cations are mono-valent and strongly hydrated ( $Na^+$ ,  $Li^+$ ), the inter-platelet repulsion is stronger and the degree of platelet separation is larger [xiii].

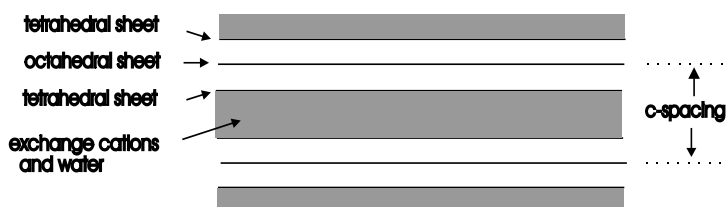


Fig. 2 Representation of three-layer expanding clay lattice.

Depending on the extent of the increase in the basal spacing between two montmorillonite sheets, two types of swelling mechanisms may be distinguished: crystalline and osmotic swelling. Crystalline swelling results from the adsorption of monomolecular layers of water on the basal crystal surfaces (on both the external and interlayer surfaces). The first layer of water is held on the surface by hydrogen bonding to the hexagonal network of oxygen atoms [xv]. Montmorillonite is capable of intercalating a number of water layers and the c-spacing increases from 10 to 20 Å [xi]. Swelling in this region is primarily due to hydration of the interlayer cations that probably take up positions between two opposing silicate layers. Van Oss and Giese [xvi] recently demonstrated, by applying a surface thermodynamic theory, that the  $\text{Na}^+$ -montmorillonite surface is hydrophilic, which also explains the large uptake of water between the platelets for this clay mineral.

Montmorillonite saturated with polyvalent cations do not normally expand beyond an interlayer separation of 10 Å, because the repulsive effect of ion hydration is offset by electrostatic attraction between the cation and silicate layers. However, montmorillonite containing small, monovalent cations, such as  $\text{Na}^+$  or  $\text{Li}^+$  can take up more water. The interlayer spacing may increase abruptly up to 30-40 Å and continues to increase to several hundred Angstroms with water content. This is called *osmotic swelling*. Its name comes from a repulsive osmotic force due to the interaction of the layers, limited only to some extent by Van der Waals forces [xi]. The repulsive force between the platelets is restrained by frictional forces arising from interactions between the particles (edge-face bonds). More recently, X-ray diffraction studies on  $\text{Na}^+$ -montmorillonite suspensions were carried out to determine the alignment of the clay particles upon swelling [xvii]. For high  $\text{Na}^+$ -montmorillonite concentrations a straight column model was used to describe the swelling behaviour observed in Norrish's work, but it failed to describe the swelling at higher water content (see Fig. 3a). A zig-zag column model was found to agree with the swelling observed at both low and high water content, where the layers swell not only longitudinally but also laterally, assuming that the layer size is 1 µm (see Fig. 3b).

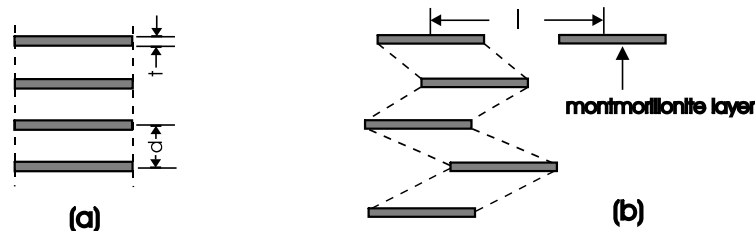


Fig. 3 Schematic diagram of straight column model (a), and zig-zag column model (b), for the arrangement of layers in montmorillonite aqueous suspensions [xvii].

## The Interactions between Clay Platelets

### Electrical double layer

Clay particles in suspension owe their stability to mutual repulsion when their interacting diffuse electrical double layers interact on approach [iii]. In clay-water systems, a double layer is made up of the negative surface charge and the balancing cation charge (Fig. 4). In the case of clay particles, the negative charge is a consequence of imperfections within the interior of the crystal lattice. Clay colloids possess a constant charge, because its surface charge arises from isomorphous substitution.

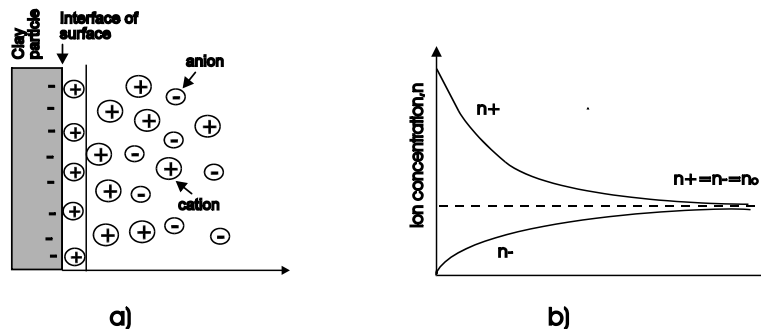


Fig. 4 a) The structure of a diffuse electrical double layer at the surface of a clay particle or silicate layer b) distribution of the concentration of cations ( $n_+$ ) and anions ( $n_-$ ) with distance from the surface for a symmetrical electrolyte with a bulk concentration of  $n_0$ .

The counter-ions are electrostatically attracted by the oppositely charged surface (Fig. 4a). These ions have a tendency to diffuse away from the surface to the bulk solution where the concentration is lower. Therefore, the concentration of the counter-ions near the particle surface is high, and it decreases with increasing distance from the surface. The diffuse layer does not only consist of an excess of ions of opposite sign; there is a deficiency of ions of the same sign near the surface, since the ions are electrostatically repelled by the surface. This



diffuse character of the counterion atmosphere was recognised by Gouy [xviii,xix] and Chapman[xx] , who presented a theoretical treatment of the counter-ion distribution. Their theory predicts an approximate exponential decay of the electrical potential  $\psi$  of the solution with distance  $x$  from the plane surface. This is represented by the following equation:

$$\psi = \psi_o \exp(-\kappa x) \quad (1)$$

where  $\psi_o$  is the surface potential and  $\kappa^{-1}$  the extension or thickness of the double layer. The above expression is valid for a certain distance from the charged surface, where the potential is relatively low and decreases exponentially (Fig. 4 b).

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_o RT}{F^2 \sum_{i=1}^n c_i z_i^2}} \quad (2)$$

where:  $F$  is the Faraday constant,  $c_i$  the electrolyte concentration,  $z_i$  the valence of the ion,  $\epsilon_o$  the dielectric constant of the medium,  $R$  the gas constant (l atm/mol K) and  $T$  the absolute temperature (K).

It can be inferred from equation (2) that as the electrolyte concentration increases, the thickness of the double layer ( $\kappa^{-1}$ ) decreases or is *compressed*. This is represented in Fig. 5 for two electrolyte concentrations or ionic strength.

Comment [PFL1]:

The surface charge of the clay particles does not change with increasing electrolyte concentration [xi], simply the diffuse double layer is compressed. The degree of compression of the double layer is governed by the concentration and valence of ions of opposite sign from that of the surface charge. The higher the concentration and the valence of the ions of opposite sign, the more the double layer is compressed. At high concentrations of sodium ( $\text{Na}^+$ ) ions where the silicate layers approach to close distances ( $\leq 10\text{\AA}$ ), the structure of the diffuse layer changes. Instead of two opposite diffuse layers of counterions between the approaching surfaces, one central layer forms and electrostatic attraction is created. Rearrangement of the counterions occurs at about 0.25 M NaCl and varies somewhat with the type of smectite [xxi]. In section 5 the type of particle associations stemming from the addition of salts will be discussed.

The Gouy-Chapman theory leads to unrealistically large ion concentrations at high potentials, since it assumes that the counterions are point charges. To correct for this, Stern<sup>xxii</sup> postulated the existence of an adsorbed layer of finite sized counterions adjacent to the surface. The potential in the Stern layer falls off linearly from its surface value ( $\psi_o$ ) to the Stern potential ( $\psi_\delta$ ), after which it decays exponentially. The thickness of the Stern layer has been estimated for different clay systems [xxiii]. The outer Helmholtz plane lies outside the Stern layer and marks the boundary between the fixed and mobile part of the diffuse double layer, and is called the *plane of shear* [xxiv.] At this plane the potential is called the zeta potential ( $\zeta$ ) and in practice it is assumed that it is equal to the Stern potential ( $\psi_\delta$ ).

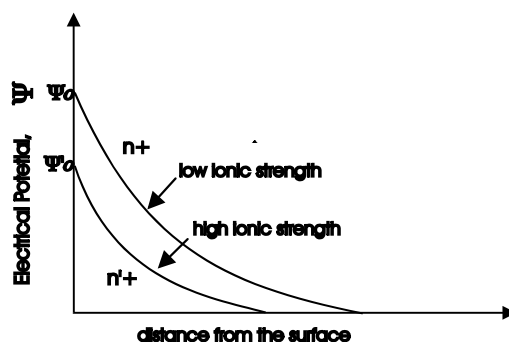


Fig. 5 Variation of the electrical potential and cation concentration with distance from the surface at low and high ionic strengths.

The edge of the clay particle is assumed to possess an electrical double layer of a different nature to that of the flat surface described above. This double layer is due to the adsorption of potential determining ions on the broken bonds of the tetrahedral silica sheets and octahedral alumina sheets. There is a strong possibility that in a neutral clay suspension a positive double layer is created on the edge surfaces owing to the exposed alumina sheet, whereby it may become more positive with decreasing pH and its sign may be reversed with increasing pH [vii]. Various studies indicate that the edges of clay particles are positively charged at pH < 7 - 8 [xxv,xxvi] and some data suggest that the edges are neutralised at pH~6 [xxvii]. The existence of positive sites on the edges have been demonstrated by the addition of a negative gold sols to the clay-type kaolinite, where the resulting electronmicrograph showed the gold particles adsorbing only at the crystal edges [xxviii].

A theoretical analysis of the interaction between colloidal particles has been developed by Derjaguin and Landau [xxix] and Verwey and Overbeek [xxx]. The fundamental feature of what is known as the DLVO Theory is that this interaction is determined by a combination of the interparticle double layer repulsion energy ( $V_R$ ) and the Van der Waals attractive energy ( $V_A$ ). Colloidal stability may be explained by means of the superposition of both energies.

-

### Interparticle Double Layer Repulsion

As two particles approach each other in suspension due to Brownian motion, their diffuse double layers begin to interfere. Consequently, there is a change in the distribution of ions surrounding both particles leading to an increase of the free energy of the system. The amount of work required to carry out those changes and to bring the particles from infinite separation to a given distance is the *repulsive energy* or *repulsive potential*.

The repulsive potential  $V_R$  between two clay platelets can be computed from the diffuse double layer theory as:

$$V_R = \frac{64\rho k_B T}{\chi} \left( \tanh \frac{ze\Psi_s}{4k_B T} \right)^2 e^{-\kappa H} \quad (3)$$

where  $\rho$  is the counterion density,  $k_B$  the Boltzmann constant,  $T$  the absolute temperature,  $\Psi_s$  the Stern layer potential,  $H$  the distance between the centre of two particles,  $e$  the electron charge and  $\chi$  the reciprocal Debye length.

$$\kappa = \sqrt{\frac{2e^2 \rho z^2}{\epsilon_o k_B T}} \quad (4)$$

The repulsive potential decreases exponentially with increasing particle separation and the range of repulsion is considerably reduced with electrolyte concentration. The DLVO theory assumes that the dispersed particles are not hydrated and hence do not have an additional repulsive force when two particles approach one another in aqueous solution. It appears likely that for  $\text{Na}^+$ -montmorillonite, the total interaction between the charged platelet surfaces should involve both short range repulsion forces, due to partially bound hydrated cations and a longer range repulsion due to hydrated counterions in the double layer [xxxi]

### Van der Waals Attractive Forces

There are three types of intermolecular attraction that are recognised: dipole-dipole interaction; induced dipole-dipole interaction and attractive forces between non-polar molecules (London dispersion forces). The London dispersion forces, which are due to the polarisation of one molecule by fluctuations in the charge distribution in the second molecule, account for nearly all of the Van der Waals attraction in colloidal systems.

The attractive energy between two semi-infinite flat plates may be expressed by the following equation:

$$V_A = -\frac{A}{12\pi} \left( \frac{1}{H^2} + \frac{1}{(H+2t)^2} - \frac{1}{(H+t)^2} \right) \quad (5)$$

where  $A$  is the Hamaker constant [xxxii] and  $H$  is the distance between the surfaces of the plates, and  $t$  is the thickness of the clay platelet. The Hamaker constant depends on the nature of the material of the particles. In the case where liquid is the dispersion medium, rather than a vacuum, this constant must be replaced by an effective Hamaker constant, calculated from the expression:

$$A = \left( \sqrt{A_2} - \sqrt{A_1} \right)^2 \quad (6)$$

where  $A_1$  refers to the dispersion medium and  $A_2$  to the particles.

#### Total Interaction Energy

The net or total interaction energy ( $V_T$ ) is the sum of the repulsive potential  $V_R$  and attractive potential  $V_A$ .

$$V_T = V_R + V_A \quad (7)$$

A representation of  $V_R$ ,  $V_A$  and  $V_T$  as a function of the interplate separation for low electrolyte concentrations ( $< 10^{-2}$  M) and high surface potentials ( $> 50$  mV) is shown in Fig. 6. Of significant importance is the occurrence of a maximum energy ( $V_m$ ) at intermediate distances, which is considered as an energy barrier that the particles must overcome if they are to “fall” into the deep primary minimum at close distances and thus come together. The height of  $V_m$  therefore determines the relative stability of the system, and a value of 15-25 kT is normally required for long-term stability.  $\Delta V_b$  represents the barrier to redispersion. At large interparticle separations, a secondary minimum may occur since  $V_R$  falls off more rapidly with increasing distances than  $V_A$ . Particle coagulation taking place here is fairly reversible, since the minimum is quite shallow.

The  $\text{Na}^+$  ions of the montmorillonite particles form diffuse ionic layers surrounding them and create an electrostatic repulsion between the particles. The addition of electrolytes in the system or an increase in temperature will reduce  $V_m$  and so the clay particles will come into contact with one another and agglomerate. The aggregation of particles is known as *coagulation* or *flocculation*. The extent to which the particles become flocculated depends upon the degree of compression of the double layer, which is dominated by the concentration and valence of the ions of opposite sign to the particle charge. Low electrolyte concentration produces *slow coagulation*, which is retarded by a long-range repulsion. At high electrolyte

concentration attraction predominates at any particle distance except at very close approach. In this case, particle agglomeration occurs at a maximum rate and the process is called *rapid coagulation*. A more detailed description of the different modes of particles association will be discussed in the next section.

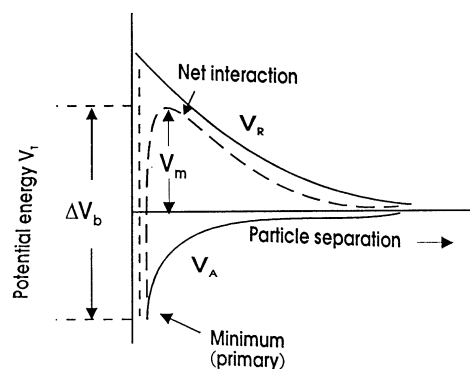


Fig. 6 Total interaction energy  $V_T$  for parallel flat plates as a function of particle (plate) separation.

### Particle Association in Clay Suspensions

If the concentration of clay is high enough, flocculation will cause the formation of a continuous gel structure instead of individual flocs. The gel structures build up slowly with time, as the particles orient themselves towards positions of minimum free energy under the influence of Brownian motion. The concentration of clay present in the system and the salt content are decisive factors in the length of time required for a gel to attain maximum strength [xxxiii]. For  $\text{Na}^+$ -montmorillonite, this concentration is usually above 3% (w/w).

When a suspension of plate-like clay particles flocculates, three different modes of particle association may occur: face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE) [xxxiv]. The electrical interaction energy for the three types of association is governed by three different combinations of the two double layers. Also, the rate of diffusion of the particles as they approach each other in these three ways is not the same, and they may not occur simultaneously or to the same extent when the clay suspension is flocculated. The various modes of particle association are illustrated in Fig. 7. FF association leads to thicker and larger flakes, and EF and EE association lead to three-dimensional voluminous “house-of-cards” structures.

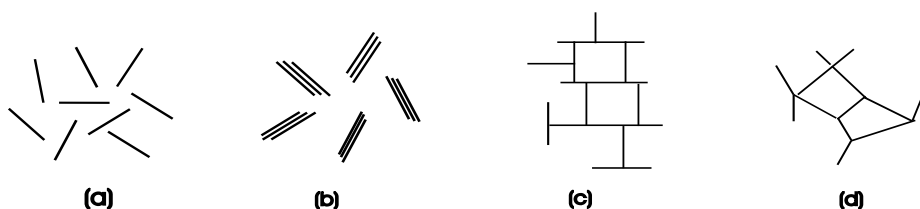


Fig. 7 Modes of particle association in clay suspensions: a) dispersed b) face-to-face (FF) c) edge-to-face (EF) d) edge-to-edge (EE) [34].

*Aggregation* is best described by FF association, and refers to the collapse of the diffuse double layers and the formation of aggregates of parallel platelets spaced 20 Å or less apart [xxxv]. It decreases the gel strength because it reduces the number of units available to build gel structures and the surface available for particle interaction. The reverse for aggregation is known as *dispersion*.

*Flocculation* of clay suspensions has been referred to as a consequence of EF and EE association, responsible for the continuous gel-like structure in the montmorillonite clay suspensions. However, other theories describing the modes of interaction between montmorillonite particles have been proposed. Including the abovementioned, they are:

- Mutual repulsion of the particles as a result of the interactions between their double layers [xi]
- Edge-to-edge association to form cross-linked ribbons, due to the high repulsive potential between basal surfaces [xxxvi] (see Fig. 8a).
- Parallel association of plates, held together by crystalline water between them [xxxvii].

Norrish [xi] opposed Van Olphen's theory of the house of cards structure, suggesting that the gel structure in montmorillonite suspensions was a consequence of the repulsive force caused between the interacting double layers. Callaghan and Ottewill [xxxviii] actually demonstrated that the gel properties of these dispersions are the consequence of long-range interactions between the faces of the particles. This theory is substantiated by the fact that the area of the edge is small, therefore the electrostatic attraction between the edge and face is small compared to the repulsion between the two faces when two particles approach each other. These authors supported more the existence of a band-like structure or the "Bänder-model" which was first proposed by Weiss and Frank [xxxix] (see Fig. 8b).

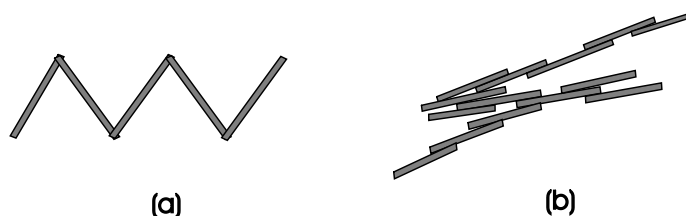


Fig.8 Alternative models describing the association of clay particles a) edge-to-edge (EE) ribbons [xxxvi], b) "Bändermodell" [xxxix].

The particle association between clay platelets determines the rheological behaviour of concentrated  $\text{Na}^+$ -montmorillonite or Bentonite suspensions. This will be discussed below.

### Influence of electrolytes and pH of the medium on particle association

In a dilute clay suspension, the particles are suspended in pure water and do not agglomerate, due to the interaction of the diffuse double layers. In the presence of an electrolyte the particles may approach each other so closely that they flocculate. The critical concentration of electrolyte at which this occurs is known as the *critical flocculation value*. The higher the valence of the cations (either on the clay or in the salt), the lower the flocculation value.

The influence of electrolyte concentration and pH on the association of montmorillonite particles has been a topic of considerable interest. At a sufficiently high clay concentration and low electrolyte content, the platelets may flex according to their relative positions and the relative magnitude of their surface and edge potentials. When the edges are positive, the platelets flex towards a negative face [xl]. When the edges are negative, the platelets are forced to assume a more parallel type orientation. For this reason, the pH of the medium is an important parameter related to the gel structure of the suspension.

The existence of an edge-to-face EF type association in montmorillonite suspensions was questioned by M'Ewan and Pratt [xxxvi], who suggested that the particles are aligned edge-to-edge EE in ribbons in the pH range 6.9-13, by conducting light scattering studies. Rand et al. [xli] supported this belief by studying the effect of NaCl on the rheological behaviour of dilute (<1% w/w)  $\text{Na}^+$ -montmorillonite suspensions and by assuming that the edge surface isoelectric point lies at a pH value below the isoelectric point of the face. Keren et al. [xxxii] determined the critical flocculation values of 0.1% (w/w)  $\text{Na}^+$ -montmorillonite suspensions in aqueous media at different pH values and found these to be 10, 13, 31 and 44 mmol/l of NaCl at pHs 5, 7.5, 8.5 and 9.8, respectively. Decreasing the pH led to lower flocculation values because the number of negative charges on the edges was reduced and increasing number of EE and EF association between edges at low negative charge and basal surfaces occurred. Additionally, the high gel volume found for dilute (0.1% w/w)  $\text{Na}^+$ -montmorillonite suspensions at pH~9.8 indicated the existence of an open three-dimensional structure, where FF

type association is predominant and the ability to trap more water between the layers than for lower pH values, where EE and EF type association prevails. Brandenburg and Lagaly [xxi] proposed that in the pH region of 5-7.5 edge-to-face (EF) contacts are destroyed due to the low positive edge charge density, basing their conclusions on rheological data for more concentrated  $\text{Na}^+$ -montmorillonite suspensions.

Stawinski et al. [xlii] studied the influence of sodium and calcium nitrate on the particle aggregate size of Bentonite. The mean aggregate radius was found to initially decrease with electrolyte concentration. Further addition of the electrolytes led to an increase of the mean aggregate radius. Scanning electronmicrographs showed that a small addition of  $\text{Na}^+$  concentration led to the formation of edge-to-edge (EE) type aggregates, whereas a more concentrated solution resulted in the formation of very compact irregular aggregates having a multilayer structure of the face-to-face (FF) type.

In summary, depending on the conditions of pH and salt concentrations, EE and EF contacts between clay particles can be formed. These contacts are usually most probable at low pH values and low electrolyte concentrations [xliii]. At a somewhat higher salt concentration, the potential between the surfaces become attractive and FF contacts are predominant. The particles then aggregate face to face to form a linked structure throughout the system [xliv]. By employing sophisticated electronmicroscopy techniques, these authors observed that with increasing  $\text{Na}^+$ -montmorillonite concentration the particles consist of face to face associations of clay platelets made-up of a few silicate layers. By the addition of a relatively high concentration of salt (0.06 M), the number and size of these aggregates are enhanced, whose thickness was estimated to be between 2 and 5 nm.

### **Electrokinetic Phenomena in $\text{Na}^+$ -Montmorillonite Suspensions**

Electrokinetic phenomena occur when two phases move with respect to each another and the interface is the electrical double layer. In the motion between the solid and liquid phase, a thin layer adheres to the solid surface and the shearing plane between the liquid and the solid is located at some unknown distance from the solid surface. Part of the counter-ion atmosphere therefore moves with the solid, and part of it moves with the liquid. The electric double layer potential at the shearing plane is called the electrokinetic or zeta potential. Electrokinetic phenomena, in particular electrophoresis, are used commonly in the studies of colloidal dispersions.

Electrophoresis occurs when an electrical field is applied to the suspension of particles. In the case of clay particles, which carry an electrical double layer charge, these move toward the positive electrode and the part of the counter-ions move to the negative electrode. The other part of counter-ions adhere to the moving particles, and are located between the clay surface and the outer boundary layer, the latter called the “slipping plane” or “shear plane”.

The zeta potential of the particle refers to the potential at the shear plane  $\zeta$ . It may be determined from measurement of the velocity of particles in an electric field  $E$ . Smoluchowski



[xlv] concluded that the relationship between particle velocity  $v$  and electric field  $E$  has the form:

$$v = \frac{E \epsilon_r \epsilon_o \zeta}{\eta_l} \quad (8)$$

and hence the electrophoretic mobility  $\mu_e$  is given by:

$$\mu_e = \frac{\epsilon_r \epsilon_o \zeta}{\eta_l} \quad (9)$$

where  $\eta_l$  is the liquid viscosity, and  $\epsilon_r$  and  $\epsilon_o$  are the dielectric constants of the medium and free space respectively. Equation 9 can be applied to a solid nonconducting particle of arbitrary shape and with curvature radius  $a$  greater than the double layer thickness ( $1/\kappa$ ) at any point of the surface. The double layer must be thin so that the following equation applies for a symmetrical electrolyte [xlvi] :

$$\frac{\exp(ze\zeta / 2k_B T)}{\kappa a} \ll 1 \quad (10)$$

The zeta potential of clay particles deduced from the electrophoretic mobility using the Smoluchowski equation has been questioned due to the heterogeneity of the particle charge. The positive charge on the edges of the platelets may screen the negative charge on the faces, resulting in a lower negative mobility. Thus the zeta potentials calculated from these mobilities cannot accurately represent the potential at the shear plane in the vicinity of the negative faces. However, a method has been proposed by Williams and Williams [xlvii] for an approximate estimation of the zeta potential for edge-type surfaces that are made up of quartz and alumina. Assuming that the potential at the edge is a linear combination of the potentials of quartz and alumina, then at pH~6-7 the edge is neutral. Since the edges of montmorillonite clay particles are similar to the former, the same concept can be applied and at this pH value the zeta potential calculated from electrophoresis is closer to that of the face surface. Delgado et al. [xlviii] used this assumption for estimating the zeta potential of Na<sup>+</sup>-montmorillonite particles from electrophoresis experiments from the Smoluchowski equation. They also used the more elaborated formulation of the zeta potential of spherical particles by O'Brien and White (1978), which takes into account double layer polarisation and surface conductance. The values of the zeta potential for the Na<sup>+</sup>-montmorillonite particles from the application of both theories were found to be very similar for NaCl concentrations of 0.001 M and above. Callaghan and Ottewill [xxviii] found that the electrophoretic mobility of Na<sup>+</sup>-montmorillonite particles is constant in the pH range (pH 3-11), as did Rioche and Siffert [xlix] for pH values between 7-11. Their results support the existence of a strong pH-independent negative charge on the clay surface,

and a much weaker positively charged double layer located on the edge surfaces of the layers. The electrokinetic properties of montmorillonite suspensions are therefore dominated by the charges on the faces.

## Adsorption of Non-Ionic Surfactants and Polymers onto Clay Surfaces

The interactions that take place between the bare clay particles in suspension are modified by the presence of polymer on the clay surfaces. Therefore, the adsorption of non-ionic polymers onto clay surfaces alters the rheological behaviour of clay/polymer suspensions. For this reason, it is important to understand the mechanism by which polymer adsorption occurs. The polymer structure, the molecular weight and its solvency in the medium influences the amount and mode of adsorption onto the surface. The mechanism and mode of adsorption of non-ionic surfactants or block copolymers (amphiphilic molecules) is different to that of non-ionic polymers, and consequently the flow behaviour for each clay system differs.

### Steric Stabilisation

Steric stabilisation of colloidal particles is imparted by macromolecules that are attached (i.e. by grafting or by physical adsorption) to the surfaces of colloid particles, preventing them from coming together or flocculating [1]. This is illustrated in Fig. 9.

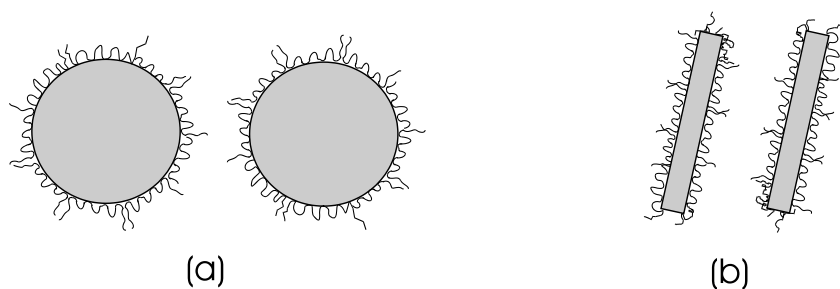


Fig. 9 Schematic representation of steric stabilisation a) spheres b) flat plates.

One of the main advantages of steric stabilisation over electrostatic stabilisation or double layer repulsion, is its relative insensitivity to the presence of electrolytes. Low amounts of electrolyte may induce flocculation of the particles, unless they are protected by the presence of polymers attached to their surfaces. Other advantages are that steric stabilisation is effective in both aqueous and non-aqueous media, and it is possible to achieve stabilisation at both low and high volume fractions of the dispersed phase. This last aspect is favourable for many practical applications that involve a relatively high volume or weight fraction of solids.

### Effect of polymer adsorption on the net energy of interaction

The adsorbed polymers on the surface of the particles have an effect on the electrical double layer interactions and on the Van der Waals interactions. In the first case, the electrical double layer repulsion will be enhanced if the stabilising agent is ionised and carries the same sign as that of the particles. As illustrated in Fig. 10, the structure of the electrical double layer is modified by the presence of “trains” close to the surface (attached portion of the polymer) which changes the thickness of the Stern plane and “loop” and “tail” segments (stabilising moieties) modifying the outer (Gouy) layer [li]. The repulsion term ( $V_R$ ) in the DLVO theory is modified by changes in the surface charge, displacement of specifically adsorbed counterions by trains and oriented water molecules, changes in the dielectric constant, thickness of the inner layer by train segments and changes in the outer layer by loops and tails [lii]. As to the effect on the Van der Waals interaction, adsorbed layers solvated in water may cause a significant lowering of the Hamaker constant, weakening the interparticle attraction.

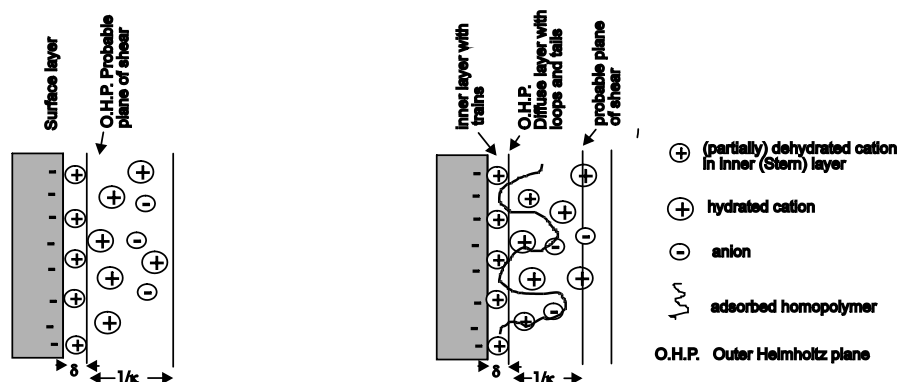


Fig.10 The effect of an adsorbed uncharged homopolymer on the structure of the electrical double layer.

When the distance between the particles is less than twice the thickness of the adsorbed layer ( $h < 2\delta$ ), the loops and tails on one surface begin to be restricted by the second surface. Thus, configurational entropy is lost. Considering the Gibbs free energy of the system ( $G_{Gibb}$ ), any change in the former is given by:

$$\Delta G_{Gibb} = \Delta H - T\Delta S \quad (11)$$

where  $\Delta H$  is the change in enthalpy in the system and  $\Delta S$  is the change in entropy. In equilibrium  $G_{Gibb}$  will seek to minimise itself and thus negative values of  $\Delta G_{Gibb}$  are favoured.

According to equation (11), a decrease in configurational entropy leads to an increase in  $\Delta G_{\text{Gibb}}$ , which is unfavourable. As a result, an elastic repulsive energy ( $\Delta G_{\text{el}}$ ) is created as a positive contribution to the potential energy.

Napper has shown that for parallel surfaces [11]:

$$\Delta G_{\text{el}} = 2k_{\text{B}} T \Gamma \ln \left( \frac{\Omega(h)}{\Omega(\infty)} \right) \quad (12)$$

where  $k_{\text{B}}$  is the Boltzmann constant,  $T$  the temperature,  $\Omega(h)$  are the available conformations at  $h$  and at  $h=\infty$  distance, and  $\Gamma$  the number of adsorbed molecules per unit area of surface.

Other than an entropic contribution to the potential energy, there is also an enthalpic contribution as a result of the local increase in the concentration of polymer molecules ( $\Delta G_{\text{mix}}$ ):

$$\Delta G_{\text{mix}} = 2k_{\text{B}} T \left( \frac{V_{\text{p}} \Gamma}{V_{\text{s}}} \right)^2 (0.5 - \chi) R_{\text{mix}}(h) \quad (13)$$

where  $V_{\text{p}}$  and  $V_{\text{s}}$  are molar volumes,  $R_{\text{mix}}(h)$  is a geometric function which depends on the polymer density distribution and  $\chi$  is the Flory-Huggins interaction for the polymer-solvent pair.  $\Delta G_{\text{mix}}$  can be either favourable or unfavourable and contribute positively or negatively to the potential energy curve. Usually a high osmotic pressure differential between the interparticle region and the bulk solution favours the situation in which there is more solvent and hence more distance between the particles.

The free energy of steric interaction ( $\Delta G_{\text{S}}$ ) is the sum of  $\Delta G_{\text{el}}$  and  $\Delta G_{\text{mix}}$ . The main parameters that determine ( $\Delta G_{\text{S}}$ ) are: the number and mass density of the stabilising species, the molecular weight of the stabilising moieties (extended polymer chains), the mode of attachment of the stabilising moieties to the particle surface, the quality of the solvency of the medium towards the stabilising moieties, the particle geometry and the net London dispersion attraction.

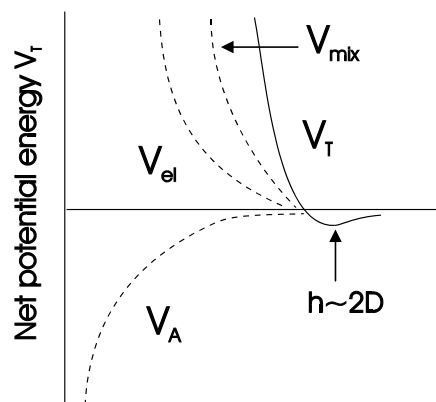


Fig.11 Schematic interaction energy diagram for sterically stabilised particles [lii].

In the case where there is high coverage of the polymer on the particles the net potential energy  $V_T$  will be the sum of:

$$V_T = V_{el} + V_{mix} + V_A \quad (14)$$

as illustrated in Fig. 11.  $V_T$  remains positive and only a shallow minimum occurs at approximately  $h \sim 2D$  (twice the polymer layer thickness  $D$ ) where  $V_A$  may be superior to  $V_{mix}$  and  $V_{el}$ . The presence of a minimum at  $h \sim 2D$  depends on the Flory-Huggins polymer/solvent interaction parameter  $\chi$ . When the polymer is in good solvency conditions,  $\chi < 0.5$  and  $V_T$  remains positive. However, if the parameter  $\chi$  is varied by the addition of nonsolvent (electrolytes) or a change in temperature or pressure such that  $\chi > 0.5$ , then  $V_{mix}$  becomes negative and  $V_T$  becomes attractive. Thus a minimum at  $h \sim 2\delta$  is displayed at which flocculation is apparent.

#### *Polymers used to impart stability*

The most common types of polymers used as steric stabilisers are block or graft copolymers [liii]. These consist of at least two chemically bound homopolymer components, one of which is soluble in the dispersion medium, while the other is generally insoluble. In an aqueous medium, the former is known as the hydrophilic group and the latter the hydrophobic group. The hydrophobic group, otherwise known as the “anchor” group, attaches itself to the colloidal particles. The hydrophilic group possesses a high affinity for the solvent, is projected away from the particle surface into the dispersion medium and is responsible for the stability of the suspension. Surfactants are also used to impart stability to a suspension. The most common type of surfactant is that comprising a polyoxyethylene oxide group  $-(OCH_2CH_2)_yOH$ , which is hydrophilic, linked to either an alkyl  $C_xH_{2x+1}$  or an alkylphenyl  $C_xH_{2x+1}C_6H_4$  hydrocarbon chain. Fig. 12 illustrates the mode of attachment of block and graft copolymers on the surface.

The attachment of non-ionic surfactants on the surface will be discussed in more detail in below.

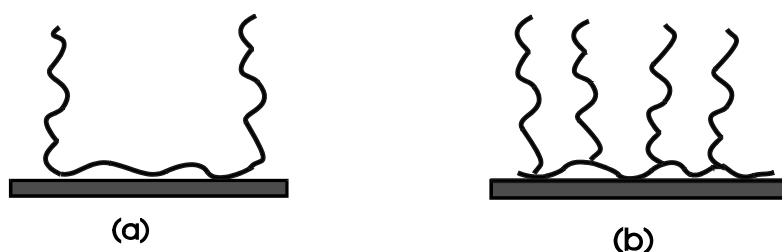


Fig. 12 a) ABA block copolymer b) AB graft copolymer

The necessary requirements for effective steric stabilisation are:

- large amount of adsorbed polymer on the surface: high degree of surface coverage;
- efficient anchoring of the polymer on the surface: strength of adsorption;
- thickness of adsorbed layer needs to be sufficiently large,  $h \sim 2D$  : extended tails and loops (when particle concentration is large);
- favourable solvent requirements for the segments in tails or loops.

#### *Flocculation of sterically stabilised suspensions*

There are basically two types of flocculation of sterically stabilised suspensions. The first is *strong flocculation* and the second is *weak reversible flocculation*. Strong flocculation results from there being a low coverage of polymer on the surface. The segments of a polymer chain are able to adsorb onto different particles linking them together, which leads to an attractive interaction between the particles ("bridging" flocculation). The result is a relatively deep energy minimum. Fig. 13 illustrates "bridging" flocculation between particles and their subsequent stabilisation.

Attachment of the hydrophobic portion of the polymer chain occurs on hydrophobic adsorbates, while for hydrophilic surfaces the attachment occurs via the polar chain. In the latter case, the surface may contain hydroxyl groups and the polymer has hydrogen bonding sites. A review by Kitchener on polymeric flocculants [liv] establishes that flocs (aggregated particles) produced with polymers are much stronger than those formed by the addition of electrolytes. The particles are held together with elastic bonds, rather than by Van der Waals forces. Nevertheless, above a critical shear rate the flocs are broken down. Effective bridging flocculation requires that the adsorbed polymer extends far enough from the particle surface to attach to other particles and that sufficient free surface is available for the adsorption of segments of the extended chains. To achieve this, there is an "optimum dosage" for producing the largest flocs where the polymer is practically all adsorbed, but the surface carries only half of the saturation capacity of the polymer ( $\theta = 0.5$ ). Healy and La Mer first established the condition of "half-surface coverage" for optimum flocculation [lv]. If more than the optimum

quantity of polymer is added, the efficiency of flocculation is reduced and the suspension may be permanently stabilised.

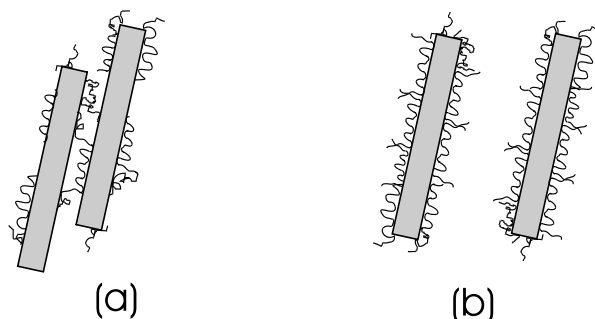


Fig. 13 Schematic representation of a) bridging flocculation b) stabilisation by adsorbed polymer

The flocculation of clays by polymers was first studied by Ruehrwein and Ward [lvi] and Michaels [lvii], who both studied the effect of charged polyelectrolytes on the flocculation of clay suspensions. Both emphasised the strong adsorption of the polymers on the clay and the concept of the formation of strong anchor points for bridges. Kitchener [liv] pointed out how in addition to charged polymers, non-ionic polyacrylamide flocculated clay particles, without the addition of electrolytes. In their view, the electrical double layer is not so strong as to prevent the particles coming within bridging range towards one another. Koksai et al. [lviii] found that kaolinite clay is flocculated by very low concentrations of polyethylene oxide of high molecular weight. In addition to finding that flocculation is enhanced at low pH and low salt content, the higher molecular weight polyethylene oxide is a better flocculant than the polyethylene glycol used. This last result was attributed to the high molecular weight PEO chain being more amenable to the formation of tails and loops that are required for bridging flocculation to occur.

The second type of flocculation is induced when either the solvent requirements for the polymer (stabilising moieties) are unfavourable ( $\chi > 0.5$ ) and/or the thickness of the adsorbed layer ( $D$ ) decreases. In this case, the total interaction energy  $V_T$  increases. Different ways to promote instability or flocculation in sterically stabilised suspensions by decreasing the solvency conditions can be achieved by: changing the temperature, increasing the pressure or by adding a miscible non-solvent for the stabilising moieties [xiii]. Accordingly, there may be a critical flocculation temperature (c.f.t.), critical flocculation pressure (c.f.p.) or a critical flocculation concentration (c.f.c.). Usually a very abrupt change from a stable dispersion to a very flocculated one occurs at these different points. A number of studies of sterically stabilised suspensions have found a correlation between the critical flocculation point and the theta (Flory) point for the stabilising moieties, which are free in solution [lix lx]. The theta-temperature corresponds to the temperature at which the polymer molecules behave as if

they were ideal small molecules and the effects of attractive and repulsive interactions balance one another out. The theta-point represents the transitional point with respect to segment-solvent interactions: the polymer segments change from exhibiting a mutual repulsion to a net mutual attraction. The theta-condition may also be achieved by the addition of a nonsolvent.

## Adsorption of Non-Ionic Surfactants on Hydrophilic Surfaces

### *The adsorption isotherm*

For very dilute solutions, the general equation of the adsorption isotherm is given to a good approximation by [ixi];

$$\Gamma = \frac{C_i \Delta x_D}{mA_s} \quad (14)$$

where  $\Gamma$  is the number of moles of surfactant adsorbed on a unit mass of insoluble adsorbent,  $C_i$  is the number of moles of surfactant in solution before adsorption,  $\Delta x_D$  is the change in mole fraction of surfactant in solution resulting from adsorption,  $m$  is the mass of insoluble adsorbent and  $A_s$  is the specific surface area of the solid.

It is possible to determine experimentally  $\Gamma$ , from the change in solution composition  $\Delta x_D$  which accompanies adsorption, and by knowing the specific surface area of the solid  $A_s$ . The change in solution composition  $\Delta x_D$ , the difference between surfactant concentration before and after adsorption, can be estimated by a number of techniques. The most common are those that determine the adsorption from solution depletion and include UV or IR absorbance, differential refractometry, surface tension and gravimetric techniques [lxii].

Giles et al. [lxiii] classified the isotherms of dilute solutions by plotting the amount adsorbed  $\Gamma$  as a function of the equilibrium concentration ( $C_{eq}$ ) for different solid/liquid systems, and distinguished four characteristic classes based upon the shape of the isotherm. The L (Langmuir) class was found to be the most common and is characterised by an initial region that is concave to the concentration axis. The subgroups of this class are related to the behaviour at higher concentrations. They are illustrated in Fig. 14.

L1 is the isotherm for low concentrations indicating a steady increase of the adsorbed amount with concentration of surfactant. The L2 type isotherm reaches a plateau at higher concentrations, meaning that full coverage of the adsorbent has taken place. Further adsorption of surfactant gives rise to the L3 type isotherm, and if a second plateau is eventually reached at a higher concentration it is designated L. In this last subgroup, the presence of the first plateau may not be detectable due to experimental insensitivity in the low concentration region. The sharp increase prior to reaching the second plateau corresponds to the bulk concentration close to the c.m.c. (critical micellar concentration).



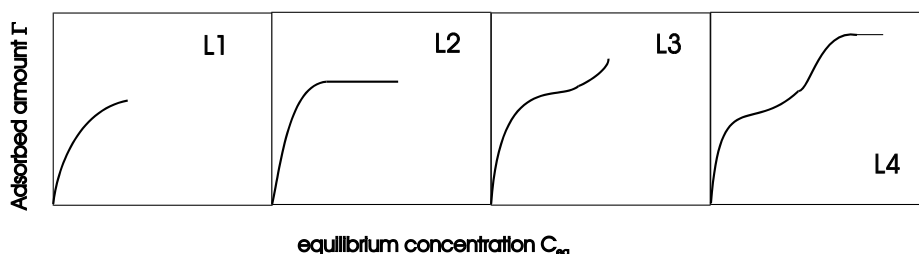


Fig. 14 Classification of the Langmuir type isotherms

Adsorbents may be heterogeneous in the sense that they contain a wide range of high to low energy sites which may be polar or non-polar, as well as associated impurities. This is the case of mineral surfaces. The shape of the isotherm largely depends on the interaction between the surface and the adsorbed species. The type of interaction may be chemical or physical, depending on the functional groups on the surface and of those belonging to the surfactant. Several types of bonding can be identified as follows: (i) chemisorption (ii) hydrogen bonding (iii) hydrophobic bonding and (iv) van der Waals forces.

#### *Mechanism of adsorption of non-ionic surfactants on hydrophilic surfaces*

Due to adsorbate-adsorbate and adsorbate-solvent interactions, non-ionic surfactants show changes in the orientation and packing at the interface as the concentration is gradually increased in bulk solution. The most general Langmuirian type isotherm (L4) shows differences in the adsorbed amount at successive stages. A scheme that shows the most likely orientation of non-ionic surfactants onto hydrophilic or polar adsorbents is depicted in the diagram of Fig. 15, in which there is a strong interaction between the adsorbent and the hydrophilic moiety of the surfactant. The numbers on the left correspond to the different stages of the adsorption isotherm in Fig. 16 [lxii].

In stage I of adsorption the main interactions that take place are adsorbate-adsorbent and adsorbant-solvent interactions. Adsorption is the result of van der Waals interactions and hydrogen bonding, the latter taking place between the polar groups of the surfactant and the functional groups present on hydrophilic surfaces. The surfactant tends to lie flat on the surface, as both hydrophobic and hydrophilic portions are positively adsorbed. In this situation, the adsorption energy increases for each additional carbon atom in its alkyl chain, as well as for each additional ethylene oxide group [lxiv]. Stage II of the isotherm is characterised by a plateau, in which the adsorbed amount reaches a steady value. At this point the surface is saturated with a monolayer of surfactant molecules lying flat.

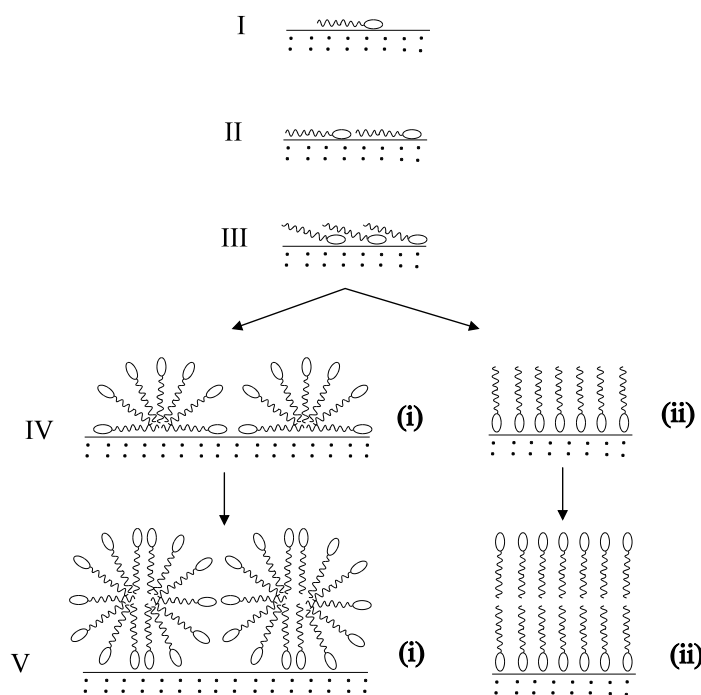


Fig. 15 Model for the adsorption of non-ionic surfactants and orientation at the interface on hydrophilic adsorbents: I -initial interaction of surfactant molecule with the surface, II -monolayer coverage by the surfactant, III -displacement of hydrophobic group of surfactant, IV (i) hemi-micelle adsorption (ii) vertical adsorption of the surfactant, V (i) micelle adsorption (ii) bilayer adsorption.

The adsorbate-adsorbate interactions become significant in stage III as the surfactant concentration is increased, and the alkyl chains become displaced. As the concentration of surfactant approaches the c.m.c., the alkyl chains of the adsorbed surfactant molecules have a tendency to aggregate (adsorbant-adsorbant interactions) and thus become vertically oriented, as depicted in stage IV(ii). In this situation the surfactant occupies less area at the interface, hence a more close packed layer is formed and there is a sharp rise in the adsorbed amount. The hydrophilic ethylene oxide chain possesses a less coiled arrangement which results in a more extended conformation at the surface. It is likely that only partial detachment of the ethylene oxide chain takes place at this stage. An alternative model would be the formation of micellar aggregates at the surface, rendering the surface hydrophilic, as in IV(i). Klimenko et al. [lxv] postulated a mechanism of surface associate formation by surfactants at the solid interface during adsorption from aqueous solution. For polyoxyethylated alkyl phenol surfactants, the concentration of unassociated surfactant molecules in a micellar solution is constant and equal

to the c.m.c. irrespective of the overall concentration in solution. They demonstrated experimentally that the formation of adsorbed surface associates at the interface takes place by a transfer of individual unassociated molecules into the surface layer. The individual molecules adsorb directly onto the interface and become centres for subsequent association.

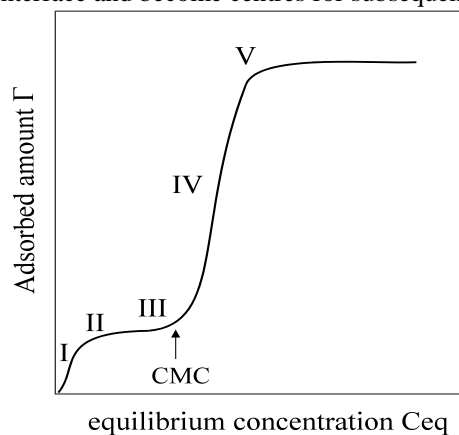


Fig. 16 Adsorption isotherm of non-ionic surfactants on a hydrophilic adsorbent. Stages I, II, III, IV and V; same as in Fig. 15.

Increasing the surfactant concentration above the c.m.c. leads to the adsorption of a second layer parallel to the one shown in stage IV, promoted by alkyl-alkyl attraction (stage V(ii)). The surface possesses now a hydrophilic character. The lateral compression of the surfactant molecules is enhanced when the alkyl chain length increases and the ethylene oxide chain decreases, increasing the amount of surfactant adsorbed on the surface. Alternatively, micelles may be adsorbed on the surface being slightly distorted as to those in bulk solution with similar aggregation numbers (V(i)).

### Non-ionic surfactant adsorption to clay surfaces

#### *Bonding mechanisms in clay/non-ionic polymer complexes*

It has been possible to study the interactions between clays and polymers by using infrared spectroscopy [lxvi]. Thin films made up of the organic molecules and the clay can be placed directly in the beam of the spectrophotometer, and the spectra of the adsorbed species may be obtained. Shifts in frequency of various diagnostic bands may then give information on the mode of binding of the organic molecule by the clay. Various interpretations are given for the nature of polymer-clay interactions. For adsorbed non-ionic polymers onto clay, three modes of interaction can be distinguished:

### Ion dipole interactions

The saturating cation on the clay surface (exchangeable cation) serves as adsorption sites for polar non-ionic molecules by ion-dipole interactions. The greater the affinity of the exchangeable cations for electrons, the higher the energy of interaction with polar groups of organic molecules capable of donating electrons. Thus, the nature of the cation is of prime importance. This type of interaction may take place from one of two forms depending on the hydration of the clay and of the nature of the exchangeable cation. Fig.17 depicts the interactions and as an example, alcohol is used as the adsorbent.

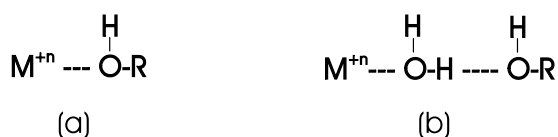


Fig. 17 Interaction between the exchangeable cation on the clay surface and an alcohol a) direct interaction b) interaction through a “water bridge”

In Fig. 17a), the alcohol ROH is directly co-ordinated to the exchangeable cation  $\text{M}^{+n}$  through the oxygen atom. In an aqueous medium or with strongly hydrated cation, the cation-alcohol link is indirect, being mediated through a water molecule in the primary shell of the cation, as shown in Fig. 17b). The latter example is known as a “water-bridge” formation.

### Hydrogen bonding

This type of bonding occurs by the direct interaction between the adsorbed molecule and the oxygens or hydroxyls of the clay mineral surface. Hydrogen bonding type interactions become significant particularly in large molecules and polymers where additive bonds due to the high molecular weight of the polymer produce a relatively stable complex. However, a very weak attraction may result for smaller molecules and in this case ion-dipole interactions become more significant. According to Mortland [lxvi], hydrogen bonding through the water bridge mechanism is often a much more important interaction in binding polar organic molecules to clay surfaces.

### Van der Waals forces

Van der Waals or physical forces operate between all atoms, ions or molecules, but are relatively weak. They result from the attraction between oscillating dipoles in adjacent atoms and decrease very rapidly with distance between the interacting species. In clay-organic compounds containing polymers of large molecular weight, these attractive forces become quite significant [lxvii].

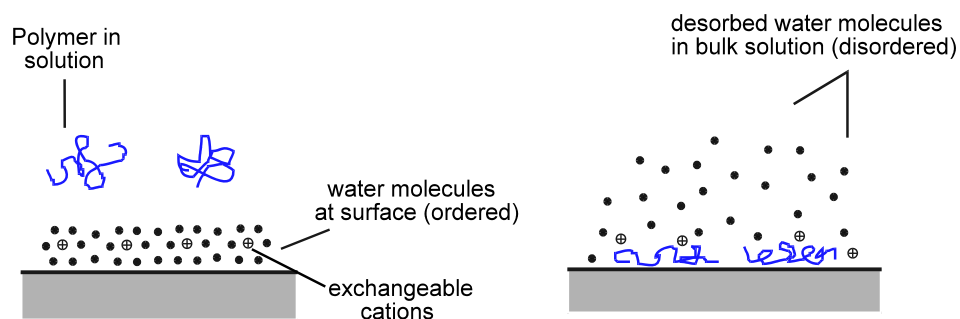


Fig. 18 Adsorption of polymers on a clay surface as an “entropy-driven” process.

### Entropy effects

The adsorption of an uncharged, flexible linear polymer onto the clay surface generally leads to the desorption of numerous solvent molecules from the surface (Fig. 18). This results in an overall increase in translational entropy contributing to the free energy of adsorption. Thus the adsorption of polymers, especially high molecular weight species, is largely an “entropy-driven” process [lxviii]. In studying adsorption of polymers on  $\text{Ca}^{+2}$ -montmorillonite, Parfitt and Greenland [lxix] observed positive entropy changes in the system when the molecular weight of the polyethylene-oxide polymers exceeded 200 g/mol. They were able to show that water was transferred from the surface to the bulk phase during the adsorption process.

### *Determination of adsorption isotherms for non-ionic surfactants onto clay*

Among the earliest studies that dealt with the adsorption of non-ionic surfactants onto clay was performed by Schott [lxx]. He determined the adsorption isotherms for  $\text{Na}^+$  and  $\text{Ca}^{+2}$  montmorillonite clay with dodecanol polyethylene oxide type surfactants of varying ethylene oxide chain length ( $n\text{EOU} = 14$  and  $30$ ) combining sample analysis and surface tension measurements. The isotherms were of the Langmuirian L4 type showing an inflection point at a value near the c.m.c., which was attributed to the formation of a single layer complex. An increase in concentration was followed by a substantial rise in the adsorbed amount, attributed to the formation of a double layer complex. When the concentration of surfactant was further increased, a small rise in adsorption was detected. It was thought that after a close-packed double layer complex is formed, the remaining surfactant was either packed between clay lamellae or randomly distributed or in voids between overlapping clay lamellae. The uptake of surfactant by  $\text{Na}^+$ -montmorillonite was greater than for  $\text{Ca}^{+2}$ -montmorillonite, the former

achieving a value of approximately 700 mg/g with respect to clay the highest concentration for the surfactant with nEOU = 1

Xu et al. [lxxi] characterised the adsorption isotherms for dodecyl octaethylene oxide surfactant onto kaolinite clay by three different regions depending on the slope: an initial hydrogen bonding of the ethoxylated groups of the surfactant with the surface; cooperative adsorbate-adsorbate interactions forming clusters on the surface; and finally a third region where the ethylene oxide chains protrude into the bulk phase. Xu et al. [lxxii] also found that there was reduced adsorption at higher pH for the same surfactant. They explained this phenomenon by the deprotonation of the surface hydroxyl groups, which decreases the number of hydrogen bonding sites available for adsorption.

A clearer understanding of the mode of adsorption of surfactants on clay was given by Denoyel and Roquerol [lxxiii], who carried out adsorption and microcalorimetric measurements of kaolinite suspensions containing octylphenol ethoxylated compounds with varying ethylene oxide chain length. Firstly, the isotherms displayed an increased affinity of the surfactant for the surface with an increase of the polar chain length. Secondly, the enthalpies of displacement showed an exothermal effect at low surface coverage followed by an endothermal effect at higher surface coverage. The authors interpreted this behaviour as an initial anchoring of the molecules (exothermal) on the surface, and a subsequent aggregation phenomena (endothermal). Thus adsorption led to the formation of micelle-like aggregates on the surface. This finding is similar to that obtained by Levitz et al. [lxxiv,lxxv], Partyka et al. [lxxvi] and Lindheimer [lxxvii] who studied the adsorption of the same type of surfactants onto silica substrates.

Röhl et al. [lxxviii] obtained adsorption isotherms for nonylphenol ethoxylated surfactants (nEOU = 6 - 15) on Na<sup>+</sup>-montmorillonite, Ca<sup>+2</sup>-montmorillonite and Na<sup>+</sup>-hectorite clay. The isotherms were Langmuirian, and a plateau was reached in all cases except for the smallest surfactant, where there continued to be a rise of the adsorbed amount. For Na<sup>+</sup>-montmorillonite, the adsorbed amount continued to rise above the c.m.c. It was observed that the adsorption of the nonylphenol ethoxylated compounds declined with an increasing degree of ethoxylation. This was explained by the fact that the interactions non-ionic surfactant/interface occur via the ethylene oxide chain by a hydrogen bonding mechanism, and hence less adsorption sites are available for the flat-adsorbed molecules.

Nevskaia et al. [lxxix] studied the effect of the ethylene oxide chain length of octylphenol ethoxylated surfactants and nonylphenol polypropylene polyethylene oxide surfactants on the adsorption onto different hydrophilic substrates, including kaolinite clay. Increasing the polar length of the chain and the number of propoxy groups led to a decrease of the adsorbed amount. Surfactants containing a longer chain length were found to adopt a "coiled-type" conformation at the surface, on the basis of experimental and theoretical calculations of the area occupied on the surface and the size of the aggregates in solution respectively. The shorter ethylene oxide chain surfactants were found to form bilayers on the surfaces. Finally, it was found that the nature of the surface determines the extent of coverage by the surfactant. For Kaolinite, for example, only 25% of the surface is covered by surfactant; higher values are achieved for the quartz samples. Thus it was considered that when maximum

adsorption is reached, the adsorption capacity of a given surface is saturated. This, however, does not imply that the entire solid surface is covered by surfactant.

## Adsorption of Non-Ionic Polymers on Clay Surfaces

### *General aspects of polymer adsorption*

In an adsorbed linear macromolecule at a surface, three types of segment sequences can be distinguished: trains, loops and tails. Fig. 19 illustrates an adsorbed polymer molecule on a surface. A train is a series of consecutive segments in contact with the surface. A loop consists of segments only in contact with the solvent, bound by a train on the surface by each side. A tail is terminally bound to a train and it dangles in solution. Depending on such parameters as the solvent quality, free energy of adsorption per segment, molecular weight of the polymer and its molecular architecture, a certain distribution of loops, trains and tails will develop.

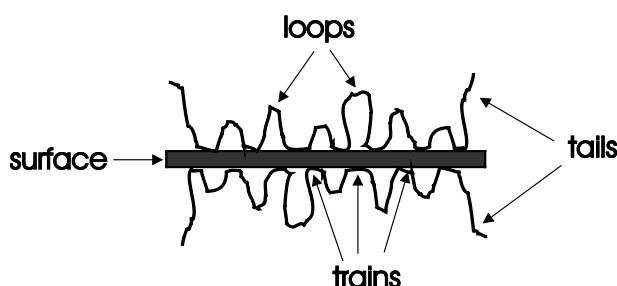


Fig. 19 Adsorbed polymer molecule

The adsorbed amount of polymer on the surface can be obtained by using equation (5). Generally, the isotherms possess a high-affinity character. High-affinity type isotherms are characterised by a very steep increase of the adsorbed amount at very low polymer concentrations, in the initial part of the isotherm [lxxiii]. Rounded-shape isotherms, mainly at the initial stage of the isotherm are related to a polydisperse polymer system, where long molecules adsorb preferentially over short ones and displace them from the surface [lxxx, lxxxi]. At higher polymer concentrations the isotherm reaches either a plateau or a pseudo-plateau. The adsorbed amount tends to increase with decreasing solvent quality and also with the molecular weight of the polymer.

A number of experimental methods have been used to study the conformation of polymers at solid-liquid interfaces. Hydrodynamic methods such as electrophoresis and photon correlation spectroscopy (PCS) have been applied to give information on the maximum extent of the polymer layer in solution. The volume fraction of the polymer segments normal to the surface has been estimated using small angle neutron scattering (SANS) and neutron reflectivity [lxxxii]. The fraction of polymer segments in direct contact with the surface (trains) can be determined by a number of methods. These techniques include infrared (IR) [lxxxiii],

microcalorimetry [lxxxiv] electron spin resonance (ESR) [lxxxv] and nuclear magnetic resonance (NMR) [lxxxvi]. ESR and NMR have been found to give higher estimates in bound fractions than IR, because the former techniques are sensitive to the mobility of the segment, while the latter is only sensitive to those moieties directly attached [lxxxvii]. The mobility of the segments that are near, but not necessarily directly attached to the surface (short loops), is reduced compared to that further away from the surface. These segments are accounted for in the NMR experiments.

A thermodynamic balance between the entropy of chains and their enthalpy determines the conformation of polymer molecules in dilute solution. The enthalpy of mixing of polymer and solvent is determined by the net polymer-solvent interaction-energy parameter  $\chi$  and the total number of polymer-solvent contacts. In a good solvent the polymer chain will expand to increase the number of polymer-solvent contacts, whereas in a poor solvent the polymer coil will contract reducing these contacts. A similar parameter is used for the interaction of a polymer segment with the surface. Silberberg [lxxxviii] has defined the adsorption enthalpy parameter  $\chi_s$  as the net enthalpy change of an exchange process, in which a segment on the surface is exchanged with a solvent molecule in solution.  $\chi_s$  is positive if a segment is preferred over a solvent molecule by the adsorbant. Additionally, adsorption will occur if  $\chi_s > \chi_{sc}$  ( $\chi_{sc}$  is the critical enthalpy for adsorption).

It is not the scope of the present review to describe in detail the theoretical models that have been developed on polymer adsorption onto surfaces. The present work is mainly concerned with experimental techniques that give directly or indirectly information of polymer adsorption onto the surface. However, it is worth mentioning some important contributions that take into account segment-surface interaction and the conformational state of the adsorbed molecule, as well as the interactions between the segments and between different molecules. They are the theoretical models presented by Scheutjens and Fleer [lxxxix, lxxxi] and de Gennes [xc].

### **Adsorption of non-ionic polymers onto montmorillonite clay**

Among the earliest studies that dealt with the adsorption of uncharged or non-ionic polymers onto montmorillonite clay was carried out by Emerson and Raupach [xci], who investigated the swelling behaviour of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  montmorillonite in the presence of a high molecular weight polymer (PVA). A portion of the prepared clay was immersed in the PVA solution and after a period of time swelling of the flakes was observed and monitored using X-ray measurements. It was observed that a low addition of PVA concentration prevented swelling of the clay. Thus the author concluded that in this case PVA was adsorbed principally on the external surfaces of the crystals, so linking them together and preventing intercrystalline swelling. Higher concentrations of PVA caused the polymer molecules to penetrate between the crystals, forming interlamellar complexes. Hydrogen bonding between PVA and the silicate surface of montmorillonite was determined to be the principal form of adsorption. This mechanism appeared to be independent of pH.



Greenland [xcii] performed adsorption measurements of PVA onto various exchanged forms of montmorillonite ( $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Cs}^+$ ). The PVA polymers were found to be strongly and irreversibly adsorbed by montmorillonite, the attachment occurring through hydrogen bonds between the hydroxyl groups of the polymers and the oxygens of the clay surface. The plateau value of the isotherm was found to decrease with increasing solids content, attributed to the polymer molecules becoming irreversibly attached to two or more clay lamellae, thereby becoming sufficiently close to restrict the access of the molecules to the surfaces. A similar behaviour was found when electrolyte (NaCl) was added to the clay/polymer suspension. The adsorbed amount of polymer was found to be larger for  $\text{Na}^+$ -montmorillonite than for the other clays, attributed to a larger basal spacing between the sheets and complete separation of the individual lamellae.

In order to obtain further information regarding the adsorption mechanism of non-ionic polymers onto clay, Parfitt and Greenland [69] studied the adsorption of a range of polyethylene glycol (PEG) polymers onto montmorillonite. The isotherms obtained for  $\text{Ca}^{+2}$ -montmorillonite varied in shape according to the molecular weight of the polymer. Polyethylene glycols up to 400 g/mol displayed a low affinity for the clay surface at low equilibrium concentrations and were linear (C type isotherms), whereas increasing the molecular weight led to Langmuir isotherms and eventually high-affinity type isotherms for molecular weight 20000 g/mol. The change from linear to L-type isotherms coincides with the change in the conformation of the molecules in solution from linear to random coil. Additionally, the adsorbed amount increased (in g polymer/g clay) with the molecular weight of the polymer. Values of the free energy of adsorption were calculated from the linear part of the adsorption isotherms and became more negative with increasing molecular weight. The entropy change became more positive with molecular weight. These results and the estimated values for the volume of water displaced from the interlamellar region, support the idea there is a desorption of water (several water molecules per adsorbed polymer chain) from the clay surface as the organic compound is adsorbed. Estimated thermodynamic values for polyethylene glycol adsorbed onto different exchanged forms of montmorillonite ( $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Al}^{+3}$ ) indicated that the direct interaction between the exchangeable cations and PEG molecules is not responsible for adsorption (ion-dipole interactions). Instead, it was proposed that the cations retain their hydration shell and that weak bonds are involved between the primary hydration shell of the exchangeable cation and that of the ether oxygen atoms of the polymer to give a “water bridge”.

Burchill et al. [xciii] demonstrated through neutron scattering studies on several exchanged forms of montmorillonite clay, that the non-coordinated water on the surface has a similar mobility to that of bulk water, but that the water coordinated to the cations is immobile on the time scale of the measurements. Thus hydrophilic polymers are able to displace the non-coordinated water and bind to the silicate surface, as well as to the exchangeable cations through the “water bridge” mechanism. The adsorption of polyethylene oxide (PEO) onto  $\text{Na}^+$ -montmorillonite gave Langmuir-type isotherms and the adsorbed amount increased with the molecular weight, similar to the results obtained by Parfitt and Greenland on  $\text{Ca}^{+2}$ -montmorillonite. Maximum adsorption for the 800, 1500 and 4000 g/mol PEO samples

corresponded to 78, 154 and 202 mg/g of clay, respectively, and the projected surface coverage for these values corresponded respectively to 26, 51 and 61% of the surface area of the clay. By fitting their results to polymer adsorption models, they inferred that PEO up to a molecular weight of 4000 g/mol adopted fully extended conformations at the surface of Na<sup>+</sup>-montmorillonite and that the sizes of the molecules prevented the development of loops to a significant extent. On the other hand, extended loops were formed on the clay with high molecular weight PVA at high concentrations.

Particularly interesting properties have been obtained for homo-ionic (Li<sup>+</sup>, Na<sup>+</sup>, etc.) montmorillonite complexes synthesised by the insertion of high molecular weight PEO [xciv]. The amount of PEO inserted remained unaltered after prolonged treatment with different solvents and was thermally stable up to 220-320°C. Above these temperatures, the intercalated material was progressively eliminated giving a collapsed phase of the initial montmorillonite. From X-ray diffraction measurements the authors concluded that the polymer adopted a flat arrangement on the surface and possessed a helical structure. Infrared measurements indicated that after intercalation of PEO there had been a significant replacement of the water on the surface. A significant enhancement of the conductivity was observed with temperature for the complex formed with Li<sup>+</sup>-montmorillonite, reaching a maximum at 300°C. Above this temperature and after PEO has been released, the characteristic conductivity of Li<sup>+</sup>-montmorillonite was attained. The properties of montmorillonite complexes formed by the intercalation of hydroxy-Al-PEO in the interlayer of montmorillonite were studied by Montarges et al.<sup>xcv</sup>. For PEO of both low and high molecular weight (600; 100,000 g/mol), the materials were thermally stable (up to 220°C) and displayed better crystallinity than the materials prepared in the absence of PEO. By thermogravimetric analysis it was possible to estimate the weight loss associated to water of the complex as a function of temperature. It was found that the intercalation of PEO replaced part of the physisorbed water during this process. For both PEO polymers, the initial sodium ions associated to montmorillonite were exchanged with the organometallic species.

In water-based drilling fluids, polyethylene glycols (PEG) have demonstrated to be effective shale inhibitors, that is, they prevent a clay cutting from dispersing in the medium (swelling) and consequently reducing wellbore problems and increasing drilling rates [xcvi,xcvii]. Cliffe et al. [xcviii] performed adsorption measurements of PEG polymers onto Na<sup>+</sup>-montmorillonite clay in the absence and in the presence of KCl. Adsorption of the PEG polymers onto the clay gave Langmuir type isotherms without reaching a plateau. However, in the presence of KCl a clearly well defined plateau was reached, indicating that condensation of the thick layers of PEG did not occur in this case. X-ray data showed that under most conditions a single layer of PEG forms on the clay in the presence of potassium, whereas in the absence two PEG layers are formed on the surface. From shale recovery tests, the complexes containing KCl and PEG were more stable in water and those without KCl or other ions (Na<sup>+</sup>, Ca<sup>+2</sup>). From these observations, the authors have given insight into the mechanisms by which PEG inhibits shale dispersion.

## Adsorbed Layer Thickness and Orientation of Polymers onto the Clay Surface

### *The orientation and thickness of the adsorbed polymer layer on the montmorillonite surface*

Most of the studies regarding the thickness of the adsorbed layer of non-ionic organic compounds on the montmorillonite surface were carried out employing X-ray diffraction techniques. Basically, a non-treated or pre-treated montmorillonite sample is soaked into the solvent (pure liquid or aqueous solutions); then the clay is washed superficially by decantation and permitted to air-dry. There may be other types of preparation as well, where the clay is immersed in the liquid during exposure. X-ray diffraction diagrams of the powder are then registered using either Fe or Cu radiation. These diagrams allowed the determination of the intersheet separation or basal spacing  $d_{(001)}$  between the clay particles. From  $d_{(001)}$  it is possible to determine the perpendicular distance between the planes containing the centres of the superficial oxygen atoms or OH groups in neighbouring surfaces of any two successive sheets. The quantity  $\Delta$  is taken as this distance less twice the van der Waals radius of oxygen. In calculating  $\Delta$ , the thickness of the montmorillonite sheet was taken as 9.4 Å, and must be subtracted from  $d_{(001)}$ . This represents the width of the space available for adsorbed molecules between the sheets, on the assumption that the van der Waals binding is operative, and that the molecules do not pack down appreciably into the hollows of the surfaces.

Greenland [xcii] determined the basal spacing between  $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{Cs}^+$  montmorillonite particles with adsorbed PVA of different molecular weight and found these to vary depending on the molecular weight of the polymer. For  $\text{Na}^+$ -montmorillonite the basal spacing was larger (16-30 Å), which was attributed the greater extent of swelling between the particles. The basal spacing  $d_{(001)}$  increased with the amount of polymer adsorbed and was found to depend on the concentration of the clay in suspension. Their results indicated that the mean depth of the polymer layer associated to each silicate layer was 10.3 Å for  $\text{Na}^+$ -montmorillonite. It was concluded that either there is a double layer of polymers between the clay sheets or that these are not completely extended on the surface. This last possibility seems to indicate that the polymer molecules are anchored to the clay by a relatively small number of segments and are extended outwards from the surface. A similar study was performed by Toyoshima [xcix] (1973) who found a mean depth of polyvinyl alcohol layer of 5 Å associated to the montmorillonite surface. He preferred the first possibility suggested by Greenland [xcii], where the adsorption of PVA on clay surfaces is unimolecular and two molecules of PVA lie between the clay platelets.

Schott [lxx] determined the basal spacings of  $\text{Ca}^{+2}$  and  $\text{Na}^+$ -montmorillonite platelets in contact with various non-ionic polymers and surfactants. The non-ionic polymers were polyethylene glycol (MW = 1000, 1500 g/mol) and polypropylene glycol (775 g/mol); the non-ionic surfactants were n-dodecanol compounds containing different number of ethylene oxide units (nEOU = 14, 30). For the polyethylene glycols and the non-ionic surfactants, the increase in basal spacing of  $\text{Na}^+$ -montmorillonite was very similar (~17.5 Å), and that of polypropylene oxide polymer being slightly higher. Thus the thickness of the adsorbed layer

was approximately (8 - 9 Å) and the author concluded that the organic molecules are intercalated with their chains parallel to the montmorillonite lamellae, in layers one or two molecules thick. It was found, however, that the non-ionic surfactants at higher concentrations adsorb onto the montmorillonite surface in excess of close-packed double layers.

The thickness of the adsorbed layer of poly(ethylene glycol) onto montmorillonite was determined by Parfit and Greenland [lxix] by X-ray diffraction techniques for different molecular weights and with varying water content. For both  $\text{Ca}^{+2}$  and  $\text{Na}^{+}$ -montmorillonite, the basal spacing increased with water content in the presence of polyethylene glycol and with molecular weight of the latter. The values for the mean depth of the adsorbed polymer layer was very similar for the two types of montmorillonite for PEO of molecular weight 20000 (~8.5 Å), and agreed with the earlier work by Schott [lxx]. It was found that extensive swelling occurred for  $\text{Na}^{+}$ -montmorillonite, despite the presence of polyethylene glycol molecules on the surfaces. More recently, Billingham et al. [c] determined the basal spacing between the  $\text{Na}^{+}$ -montmorillonite platelets with varying concentrations of low molecular weight polyethylene glycol (PEG). Throughout the entire concentration range, a spacing of 16 Å was obtained for PEG of molecular weight 300 g/mol, corresponding to 1 layer of molecules lying flat between the clay lamellae. The higher molecular weight PEG (1000 g/mol) gave the same value at low concentration. When the concentration of the latter polymer was increased, the basal spacing increased to 18.6 Å, corresponding to 2 layers of PEG lying flat between the sheets. Thus, increasing the molecular weight led to the possibility of adsorbing more than 1 layer on the surface.

Platikanov et al. [ci] determined the basal spacing of montmorillonite platelets with non-ionic surfactants of the type alkyl polyglycol ethers with varying alkyl chain length and ethylene oxide chain length ( $\text{nEOU} = 2 - 20$ ). In comparison to the previous work of the thickness of the adsorbed layer of PVA and polyethylene glycol on montmorillonite, these were significantly larger. For the different series of surfactants, the thickness of the films were between 27 -30 Å. The authors concluded that the alkyl chains form bimolecular layers and are fully extended and stand perpendicular to the silicate layers, along with approximately half of the polar end group. The basal spacing between the montmorillonite platelets with surfactant was also monitored as a function of temperature (0-110°C). A temperature dependent phase transition  $T_{\beta/\alpha}$  was observed, where a dramatic decrease of the basal spacing occurred followed by a stepwise decrease of the distance between the montmorillonite platelets. This was attributed to the surfactant molecules being squeezed out of the interlayer region, having reached the melting point of the corresponding alkanols.

Weiss [cii] (1980) extended the work performed by Platikanov et al. [ci] by identifying five stable structures and two 2-phase regions of the montmorillonite/surfactant complexes depending on the temperature. A detailed description was given in relation to the orientation of the surfactant molecules for each structure, which was found to depend on the surface area of the n-alkyl chain on the surface. According to their analysis, for complete surface coverage below the  $T_{\beta/\alpha}$  phase transition temperature, the surfactant chains are more or less perpendicular to the solid surface. Above the  $T_{\beta/\alpha}$ , tilting of the chains and desorption of the amphiphile occurred, and higher adsorption densities were found.

Röhl et al. [ciii] determined the basal spacing between  $\text{Na}^+$ -montmorillonite platelets with nonylphenol ethoxylated surfactants (nEOU = 6 - 15) by X-ray diffraction in the dry state as well as in suspension. The basal spacing obtained in suspension was considerably higher than in the dry state, confirming that after drying, the orientation of the adsorbed surfactants on the clay surface had changed. As an example, the spacing between the platelets containing a nonylphenol ethoxylated was 1 and 5.8 nm, in the dry state and in the suspended state respectively. In the latter case, this corresponded to a thickness of the surfactant of approximately 5 nm. They concluded that the surfactant was arranged diagonally to the surface in suspension, whereas in the dry state they formed densely packed double layer arrangements. Additionally, increasing the degree of ethoxylation led to higher values.

## Rheological Behaviour of Clay Suspensions

### Flow Behaviour of Suspensions

The flow behaviour of any system is described in terms of the relationship between the *shear stress*  $\tau$  and the *shear rate*  $\dot{\gamma}$ . The shear rate is defined as the change of shear strain per unit time, and the shear stress as the tangential force applied per unit area. The ratio of shear stress  $\tau$  to shear rate  $\dot{\gamma}$  is called viscosity  $\eta$ :

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (16)$$

hence  $\eta$  is a measure of the resistance to flow of the fluid.

The plot of the shear stress versus the shear rate is called a consistency curve. Four different types of flow may be distinguished: Newtonian, pseudoplastic, Bingham plastic, and dilatant, as illustrated in Fig. 20. When the shear stress is directly proportional to the shear rate, the fluid is Newtonian and exhibits a constant viscosity. In the other types of flow behaviour, the viscosity varies with the shear rate and these are called non-Newtonian fluids.

Aqueous clay suspensions that possess a relatively high particle concentration have been described traditionally in accordance to the Bingham theory of plastic flow [civ]. The Bingham model postulates that a finite stress must be applied to initiate flow and at greater stresses the flow will be Newtonian (Fig. 20). The resistance of the suspension to flow can therefore be considered as consisting of two parts: a Newtonian part in which the shear stress is proportional to the shear rate and a non-Newtonian part in which the shear stress is constant irrespective of the shear rate. The equation for the Bingham model is:

$$\tau = \tau_B + \eta_{pl}\dot{\gamma} \quad (17)$$

where  $\eta_{pl}$  is the plastic viscosity, defined as the slope of the curve, and  $\tau_B$  is the Bingham yield stress normally taken as the intercept of the flow curve at high shear rates.

Very dilute clay suspensions or drilling fluids that contain polymers behave as pseudoplastic fluids, which may be described by the power-law equation [cv]:

$$\tau = K\dot{\gamma}^n \quad (18)$$

where  $K$  is a measure of the consistency of the fluid; and  $n$  the flow-behaviour index, which is a measure of the decrease of effective viscosity with shear rate. Other models have been considered in describing the rheological behaviour of clay suspensions, such as the Casson equation [cvi]:

$$\tau^{1/2} = k_o + k_1\dot{\gamma}^{1/2} \quad (19)$$

and the Herschel-Bulkley equation [cvii]

$$\tau = \tau_y + K\dot{\gamma}^n \quad (20)$$

Both equations (19) and (20) have been used to describe the consistency curves of drilling fluids, with the Herschel-Bulkley equation being the most suitable [cviii]. In both cases, the suspension has an initial yield stress at low shear rates, and afterwards presents pseudoplastic or “shear-thinning” type behaviour at higher shear rates. In the last case, the viscosity decreases with shear rate.

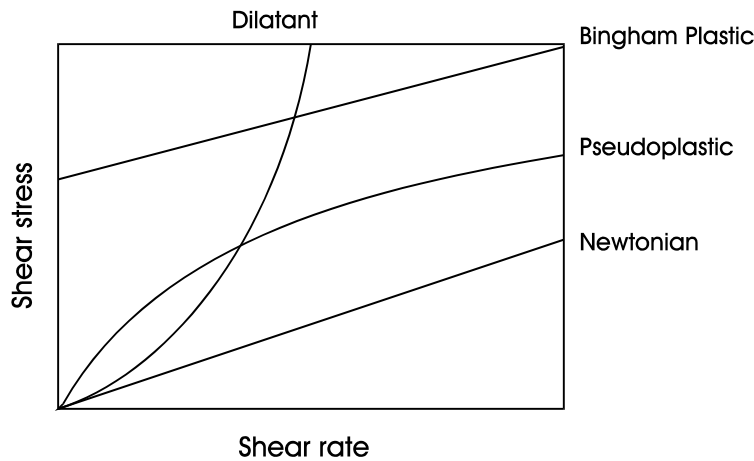


Fig. 20 Consistency curves for four different types of flow.

The parameters of the above equations may be divided between two groups [cix]. The first group, the Bingham yield stress, consistency coefficient and Casson yield stress are affected by changes in the low shear properties. In the second group, the plastic viscosity,

flow-behaviour index and the Casson viscosity, reflect the high shear rate behaviour of the fluid.

Clay suspensions frequently show a time dependent flow behaviour, known as *thixotropy* [cx]. After mixing the suspension, the yield stress and plastic viscosity decrease (Fig. 21) but will recover with time if left standing. Curve 1 represents the original flow behaviour and after mixing the suspension displays a flow behaviour represented by curve 2. After a period of rest, the initial curve 1 will be obtained. Concentrated clay suspensions are very sensitive to shear and their rheological properties will vary during the determination of the rheogram (shear stress versus shear rate). If the shear rate is ramped-up and then immediately ramped-down, the stresses recorded for each rate of shear will be lower and a “hysteresis loop” is obtained (curve 3). This occurs because the fragments of the network which are broken under shear, need time to be linked again to a three dimensional network. In addition, when the clay system is subjected to a constant rate of shear, the viscosity decreases with time as the gel structure is broken down, until an equilibrium viscosity is reached. In view of their shear and time dependency, the clay suspensions require the same preparation, handling and measurement conditions if comparisons are to be made between the rheological properties of different samples

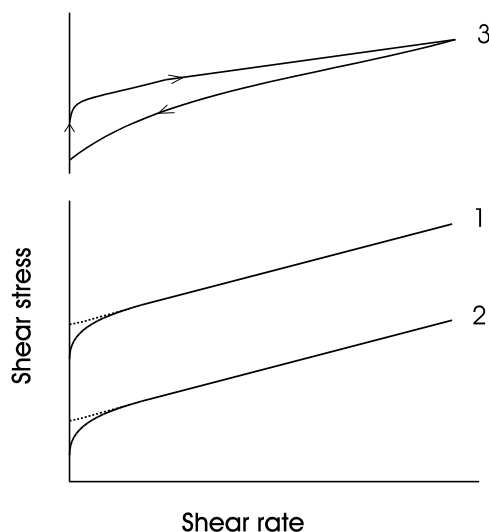


Fig. 21 Typical flow curves for concentrated thixotropic clay suspensions.  
1- initial flow curve, 2- flow curve after mixing, 3- thixotropic loop

Various factors affect the flow behaviour of clay suspensions. Naturally, the clay concentration will bring about an increase of all rheological properties. Due to the negative particle charge and double-layer structure, the yield stress and viscosity change with variations

of the pH of the suspension and electrolyte concentration. Also, differences in the rheological properties are observed depending on the type of electrolyte in solution and on the nature of the exchangeable ions. A rise of the temperature increases the interparticle attractive forces, which in turn, leads to enhanced particle-particle interactions affecting the yield stress and suspension viscosity. The suspension viscosity also depends to a great extent on the viscosity of the medium, which is also a function of temperature. Pressure effects may also alter the flow properties on clay suspensions, due to the exponential increase of liquid viscosity with pressure and the differential compression of clays and liquids. The aforementioned variables which bring about changes of the rheology of clay suspensions is discussed below, where a review of the rheological behaviour of Na<sup>+</sup>-montmorillonite suspensions is given both in the absence and in the presence of non-ionic polymers.

### Viscoelasticity

An alternative procedure for investigating the stability/flocculation of concentrated dispersions is through viscoelastic measurements [cxi]. Several studies have been carried out determining the viscoelastic properties of Na<sup>+</sup>-montmorillonite suspensions under varying conditions of pH, salt content and polymer dosage; as will be reviewed briefly in this section. Basically, these studies provide qualitative information on the gel strength of clay suspensions, on the gelation mechanism and on the possible structures that are formed in montmorillonite suspensions.

#### *Oscillatory shear*

The methods of measurement of viscoelastic properties include oscillatory experiments, which measure the response of viscoelastic materials to small-amplitude oscillatory shear. When a small amplitude sinusoidal oscillation (strain or stress) is applied to the system, the stress is compared with the strain with time. For a viscoelastic suspension, the stress oscillates with the same frequency but out of phase with the strain. By measuring the time lag of frequency  $\Delta t$ , it is possible to obtain the phase angle shift  $\delta$ :

$$\delta = \Delta t \omega \quad (21)$$

where  $\omega$  is the frequency in radians per second. The frequency is given by:

$$\omega = 2\pi \nu \quad (22)$$

where  $\nu$  is the frequency in Hertz.

In oscillatory shear, a complex shear modulus  $G^*$  is defined through the equation:



$$\tau(t) = G^*(\omega)\gamma(t) \quad (23)$$

where  $G^*$  may be a function of the oscillation frequency  $\omega$ .

For an applied oscillatory strain, the stress will possess a similar form, but its phase will be in advance of the strain by an angle of  $\delta$ . In this case:

$$\gamma(t) = \gamma_o \exp(i\omega t) = \gamma_o \sin \omega t \quad (24)$$

$$\tau(t) = \tau_o \exp[i(\omega t + \delta)] = \tau_o \sin(\omega t + \delta) \quad (25)$$

$\gamma_o$  is the amplitude of the imposed strain and  $\tau_o$  is the amplitude of the sensed stress. For a perfectly elastic system, the stress is exactly in phase with the strain ( $\delta = 0$ ), whereas for a perfectly viscous liquid, it is exactly out of phase with the strain ( $\delta = 90^\circ$ ). For viscoelastic systems, the phase angle shift lies between these limiting cases. From equations (21), (22) and (23); the following expressions can be derived:

$$G' = |G^*| \cos \delta \quad (26)$$

$$G'' = |G^*| \sin \delta \quad (27)$$

$$G^* = G' + iG'' \quad (28)$$

where  $i = \sqrt{-1}$ .

$G'$  and  $G''$  represent the *elastic modulus* and *loss modulus*, respectively. The elastic modulus  $G'$  is that part of the modulus that is in phase with the strain, and is a measure of the energy stored elastically during a cycle of deformation. The loss modulus  $G''$  is the part of the modulus that is out of phase with the strain and gives a measure of the energy dissipated in a cycle, it represents the viscous component.

### **The Rheological Behaviour of Na<sup>+</sup>-Montmorillonite Suspensions**

*Na<sup>+</sup>-montmorillonite suspensions in the absence of polymer*

Effect of electrolytes on the rheological properties and particle association

The rheological experimental work carried out by Van Olphen [cxii] indicated that concentrated  $\text{Na}^+$ -montmorillonite suspensions behaved according to the Bingham model. A very low amount of NaCl led to a decrease of the yield stress and viscosity, while higher amounts increased both of these values gradually. The results were explained in terms of the charges on the clay platelets, which were assumed to be positive on the edges and negative on the faces. Initially, edge-to-face (EF) type association occurs owing to the opposite charge attraction, which results in “internal mutual flocculation”. Upon the addition of small amounts of salt, the double layers are compressed and the effective charge determining the electrostatic attraction between edges and faces is reduced. This results in the network breaking down, accompanied by the lowering of the rheological properties. However, further compression of the double layers by increasing the salt concentration restores the edge-to-face attraction, which is now greater than the face-to-face repulsion. In this region the rheological properties were found to increase. At very high salt concentrations the yield stress of the suspensions tended to decrease, as a result of face-to-face (FF) association and the formation of thicker particles by which the number of links within the clay structure is reduced.

Other authors have supported the different types of particle associations described in the Van Olphen’s work [cxii] for  $\text{Na}^+$ -montmorillonite suspensions. Khandal and Tadros [cxiii] attributed the high value of the elastic modulus  $G'$  in these suspensions within the pH range 5 - 5.5 to EF type association; and the reduction of  $G'$  at even lower pH to FF association, due to the high electrolyte content. On studying the influence of different electrolytes on the  $G'$  values of  $\text{Na}^+$ -montmorillonite suspensions, Miano and Rabaioli [cxiv] associated the flocculated structure to EF association. A transition was found from EF to FF association with increasing electrolyte content.

However, Callaghan and Ottewill [xxxviii] gave a different interpretation to the structure development in clay suspensions. They supported the argument that the electrical double layer forces are responsible for the gel formation in  $\text{Na}^+$ -montmorillonite suspensions, initially proposed by Norrish [xi]. Rand et al. actually found no evidence for EF association of  $\text{Na}^+$ -montmorillonite suspensions within the pH range 4 - 11, but rather supported the existence of FF and EE flocculated structures [cxv]. The increase of the Bingham yield stress, plastic viscosity and shear modulus with increasing clay and salt content was attributed to the latter type of associations. They defined the shear modulus as a measure of the repulsive force between the particles due to the interpenetrating electrical double layers.

The experimental work carried out by Vali and Bachmann [cxvi] helped to elucidate the type of structure of  $\text{Na}^+$ -montmorillonite and smectite that was formed under certain electrolyte conditions, by combining electronmicroscopy and flow behaviour of the clay suspensions. Samples for electronmicroscopy were prepared using fast rate cooling techniques, such as spray or jet freezing to preserve the original structure of the suspension, which is destroyed under conventional drying techniques. The clay suspensions generally possessed a FF aggregated and partially overlapped structure of sheets that are twisted, bent and branched; whose number per unit area increases at high concentration (~3% (w/w)). They observed fewer EF and EE contacts. This structure was responsible for the developed Bingham yield stress and slight thixotropy. Addition of NaCl produced a network of larger aggregates that appeared thicker in

size, and the resulting flow behaviour showed a substantial increase of the yield stress with significant thixotropic behaviour. In summary, their work clearly supports the “band-type” aggregate model postulated by Weiss and Frank [xxxix].

The “band-type” aggregates formed predominantly by FF aggregation of the  $\text{Na}^+$ -montmorillonite particles was also supported by Bradenburg and Lagaly [xxi] and Lagaly [xlili]. The authors found a substantial increase in the shear stress values at alkaline pH with the presence of  $\text{Ca}^{+2}$  ions in the  $\text{Na}^+$ -montmorillonite lattice. This effect was explained by the  $\text{Ca}^{+2}$  cations forming a central layer between platelets, thereby creating an electrostatic attraction and promoting quasicrystalline structures. The result was thought to be face-to-face (FF) aggregation leading to thicker particles and overlapping to form “band-type” particles forming a voluminous network. Yet, the presence of  $\text{Na}^+$  ions in the montmorillonite lattice has been found to be a necessary condition for the development of a yield stress in these suspensions. Keren [xxxi] demonstrated that for both  $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$ -montmorillonite suspensions, the flow behaviour changes from Newtonian to pseudoplastic upon the addition of  $\text{Na}^+$  as the exchangeable cation, exhibiting a yield stress and an increased viscosity. This was attributed to the presence of  $\text{Na}^+$  ions which break down the clay aggregates into smaller units.

Various authors under different conditions have performed a scaling analysis of the elastic modulus with clay concentration. Callaghan and Ottewill [xxxviii] estimated the elastic modulus for  $\text{Na}^+$ -montmorillonite suspensions in the presence of very low salt concentration under compressive conditions by determining the internal pressure between the clay platelets as a function of clay and electrolyte concentration. A linear trend was found from a log-log plot of the elastic modulus as a function of clay concentration, and the equivalent exponent or power law index was found to be  $n = 4$ .

On investigating the swelling behaviour of  $\text{Na}^+$ -montmorillonite suspensions with a clay content at different pH values, Khandal and Tadros [cxiii] found that the elastic modulus  $G'$  increased exponentially with time and with clay content. A power-law index of  $n = 4 - 5$  was determined throughout the pH range. This value was related to a flocculated clay structure. Sohm and Tadros [cxvii] conducted a similar study to the former using a commercial  $\text{Na}^+$ -montmorillonite clay suspension, and found the elastic modulus to be significantly higher at different clay concentrations and at similar pH. The higher  $G'$  values were attributed to a higher degree of dispersion of the platelets in water which tends to increase the number of clay platelets. A lower power law index was obtained  $n = 7$ , reflecting an increase of the number of contacts within the suspension. It was concluded that the swelling behaviour of  $\text{Na}^+$ -montmorillonite depends to a large extent on the treatment to which it was subjected previously.

Miano and Rabaioli [cxiv] associated a power law index of  $n = 8.2$  to a stable  $\text{Na}^+$ -montmorillonite clay suspension of extended double layers on the particles with low NaCl content (0.005 - 0.01 M). A further increase of salt ( $C \geq 0.05$  M) led to lower values of  $n = 7 - 9$  and higher  $G'$  values indicating flocculation. Power-law indexes  $n$  and coefficients  $K$  were estimated for the clay suspensions in the presence of other electrolytes ( $\text{CaCl}_2$ ,  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ ). For the other electrolytes, flocculation occurred at lower concentrations and presented similar  $n$  values.

### Influence of Electrolytes on shear reversibility

Di Maio and Fenelli [cxviii] measured the residual shear strength of very concentrated  $\text{Na}^+$ -montmorillonite suspensions (25 - 100% w/w) in the presence of NaCl solutions and their microstructure (after shearing) was observed by scanning electron microscopy (SEM). The residual strength of the clay samples increased significantly with an increase in salt concentration and reached its maximum value when saturated with NaCl solution. This behaviour was found to be reversible. Time-compression curves and void ratio determination demonstrated that the addition of salt produced a noticeable volume change, a decrease of both the former values. Inward diffusion of salt towards the clay was thought as the primary mechanism for the volume and rheological changes that were produced. SEM analysis showed that the clay sample subjected to shear was composed of thin and smooth layers, strongly oriented in the direction of shear. In the presence of salt, the layers appeared to be more strongly associated into a network.

The previous study was extended to investigate the effect of adding different electrolytes ( $\text{CaCl}_2$  and  $\text{KCl}$ ) on the residual shear strength and shear reversibility, particle structure and volume changes of  $\text{Na}^+$ -montmorillonite suspensions [cxix]. The samples exposed to the electrolyte solutions increased their residual strength and reduced their volume, in a similar way to the suspensions containing NaCl. However, when reexposed to water, their shear strength did not change very much even after months of water renewal and shearing. X-ray diffraction results showed that  $\text{Na}^+$  originally present as the exchangeable ion had been substituted by  $\text{Ca}^{+2}$  or  $\text{K}^+$ , converting the original  $\text{Na}^+$ -montmorillonite into  $\text{Ca}^{+2}$ -montmorillonite or  $\text{K}^+$ -montmorillonite. SEM micrographs revealed that when exposed to a  $\text{KCl}$  solution, thick and stiff particles were formed. The author concluded that the difference in the osmotic phenomena of the clay between various electrolytes was due to the size of the hydrated ion radius. According to the Stern model, the thickness of the diffuse double layer decreases with decreasing hydrated ion radius. Since the radius of hydrated  $\text{K}^+$  and  $\text{Ca}^{+2}$  is smaller than that of  $\text{Na}^+$ , the thickness of the  $\text{K}^+$  or  $\text{Ca}^{+2}$ -montmorillonite double layer is smaller than  $\text{Na}^+$ -montmorillonite. This means that montmorillonite possessing  $\text{Ca}^{+2}$  and  $\text{K}^+$  as exchangeable cations are less sensitive to osmotic phenomena than the clay containing  $\text{Na}^+$ .

The results found previously are in agreement with the study performed by Denis et al. [cxx], where swelling and compaction curves for  $\text{Na}^+/\text{K}^+$  montmorillonite were not reversible and swelling was inhibited with increasing  $\text{K}^+$  exchange fraction. The authors investigated the effect of substituting  $\text{K}^+$  ions for  $\text{Na}^+$  ions in the montmorillonite clay matrix and performed X-ray diffraction measurements at controlled humidity and compaction/swelling experiments at different pressures. The former provided equilibrium interlayer spacings and from the latter it was possible to estimate the equilibrium void ratio at each pressure. The spacing between the clay platelets decreased with increasing  $\text{K}^+$  fraction when the relative humidity was above a certain level, and the extent of swelling was strongly inhibited in montmorillonite having  $\text{K}^+$  exchange fractions  $\geq 0.67$ . The swelling and compaction curves showed that the void ratios were generally lower for the swelling curve (after compaction) and were flatter for a  $\text{K}^+$  fraction above 0.3

### *Na<sup>+</sup>-montmorillonite suspensions in the presence of polymers or surfactants*

Schott [cxxi] measured the relative viscosities for very dilute Na<sup>+</sup>-montmorillonite suspensions in the presence of an alkyl ethoxylated surfactant, a nonylphenol ethoxylated surfactant and a polyethylene glycol. A decrease of the viscosity was found with an increase in polymer concentration in all cases. The reduction of the viscosity was attributed to deflocculation of the clay particles or their breaking up into thinner flakes. A minimum value was found, which was interpreted as the completion of a double layer complex between the particles. Beyond this value, a slight increase of the viscosity was detected for the suspensions containing the surfactant. This was thought to be due to the appearance of micelles, acting as crosslinks between the particles. Although it was observed from turbidimetric data that a higher quantity of surfactant adsorbed onto clay, the adsorbed amounts were not estimated and a clear adsorption mechanism was not given.

Kuznetsova and Serb-Serbina [cxxii] determined the structural strength or static yield values for very concentrated Bentonite suspensions as a function of polyvinyl alcohol (PVA) concentration. A very large increase of the static yield value was found with low amounts of PVA, thereafter it decreased. The maximum was attributed to a coagulation of clay particles due to the adsorption of PVA, producing a stronger network which increased with clay concentration. Further adsorption of PVA led to a decrease of the static yield, which was believed to be due to water separating out of the aggregated structure giving rise to a less compact network structure. A difficulty arising in the present study was due to very large differences of the clay content between the adsorption experiments and static yield measurements. It was not possible to correlate between the amounts adsorbed and the changes observed in the structural strength with PVA content. Also, the decrease in static yield after a maximum was attained was attributed to water separating out, rather than interpreted as a reduction of particle interactions, which is actually responsible for the strength of the suspensions.

Heath and Tadros [cxxiii] investigated the effect of adding PVA to 4% (w/w) Na<sup>+</sup>-montmorillonite suspensions on the Bingham yield stress, plastic viscosity and shear modulus. A maximum was observed for the shear modulus and Bingham yield value with the small addition of PVA, and was 30 times higher than the initial value for the latter case. A two-fold increase was found for the plastic viscosity. From determination of the adsorption isotherm, the maximum value corresponded to 1/4 full coverage of PVA on the clay particle. The increase in gelation or flocculation was attributed to "bridging flocculation" (see Section 3, section 1.3). The flocculated structure did not show any thixotropy, and it was suggested that the structure formed was rigid and irreversible, not easily destroyed when subjected to shearing conditions. Further increase of PVA content led to stabilisation of the suspension and a decrease of the rheological properties, until a constant value was reached which corresponded to maximum coverage of the adsorption isotherm.

A scaling analysis was applied [cxiv, cxv] to investigate the effect of commercial polyelectrolytes on the stability of Na<sup>+</sup>-montmorillonite suspensions (1.5 - 5% w/w) in the presence of 0.1 M NaCl. The addition of FeCr-lignosulphonate and polyacrylic acid to the

suspensions increased the  $n$  values to 9 and 5 respectively to those suspensions flocculated with salt ( $n = 8$ ), therefore stability was at least partially restored. The higher value for  $n$  in the latter case was attributed to selective adsorption of the polyacrylate polymer on the edges of the particle, therefore weakening the edge-to-face (EF) association between the clay platelets. A more effective stabilisation was viewed through the complete saturation of polymer on the surface, which in the present case was not achieved using the polyelectrolytes.

### High Pressure - High Temperature Rheology of Na<sup>+</sup>-Montmorillonite Suspensions

A very important application of clay suspensions is their use as drilling fluids in the oil industry. Among the many functions that the drilling fluids must possess to be successful at a drilling operation are to: carry the drilled cuttings and transport them back to the surface; suspend the drilled cuttings when the circulation is stopped; cool and clean the bit; reduce the friction between the drilling string and the sides of the hole; prevent the inflow of fluids from the permeable rocks that are penetrated; maintain the stability of the wellbore; and form a thin, low permeability filter cake ("mudcake") which seals the pores and other openings in formations penetrated by the bit. The main parts of the wellbore and circulation of the drilling fluid is illustrated in Fig. 22.

The fluid is pumped down the drillstring and through the nozzles in the drill bit, which dislodge rock cuttings from the bottom. The fluid then flows up the annulus between the drillstring and the rock. The clay suspension carries the cuttings to the surface, where the cuttings are separated (not shown). Afterwards, the clay suspension is recirculated. During circulation of the fluid around the wellbore, strain rates may vary from zero to approximately  $1000\text{ s}^{-1}$ . Also, temperature and pressure variations take place and may reach values in excess of  $200^\circ\text{C}$  and 1000 Bar respectively. The viscosity of the fluid can be significantly affected by these conditions.

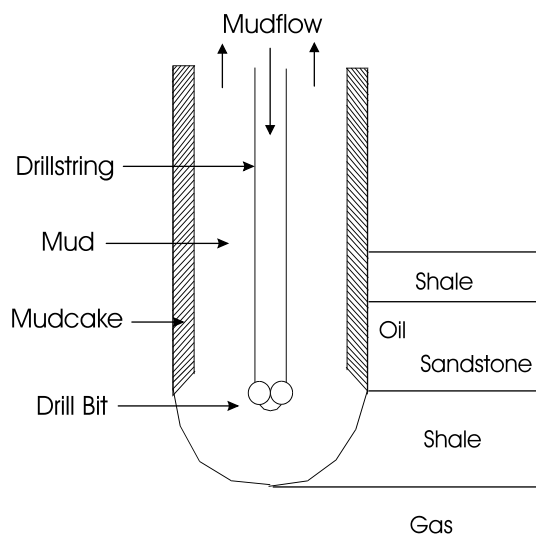


Fig. 22 Circulation of a drilling fluid through the wellbore.

Bentonite or  $\text{Na}^+$ -montmorillonite clay is a key component in the drilling fluids that possess water as the continuous phase, otherwise known as “water-based muds”. At low solid content (4 - 5% w/w) they are able to form a gel-like structure which is necessary for carrying the drilled cuttings and to suspend them when circulation of the drilling fluid is stopped. Moreover, due to the shear thinning behaviour of the fluid, a sufficiently low viscosity may be achieved at high shear rates which enables the transportation of the cuttings back to the surface. However, the composition of drilling fluids is quite complex, as they frequently possess other additives for specific functions. The addition of a high-density component such as barium sulphate is often necessary to maintain the downhole hydrostatic pressure and are held in suspension by the Bentonite clay. Water-soluble polymers may be used for either flocculating the drilled solids, viscosifying the drilling fluid or acting as an aid to filtration control. The flow behaviour of these complex systems is crucial for the efficiency of the drilling operation. The characterisation of the rheological behaviour of the fluids under conditions of high temperature and high pressure reflects the behaviour during circulation in the wellbore. In the next section the most relevant studies performed in this area will be described.

#### *High pressure - high temperature (HPHT) rheology of $\text{Na}^+$ -montmorillonite suspensions*

Hiller [cxxxv] investigated the effect of temperature and pressure on the rheological behaviour of  $\text{Na}^+$ -montmorillonite suspensions and other drilling fluids using a HPHT rheometer (Couette viscometer). Temperatures up to  $\sim 160^\circ\text{C}$  and the pressures up to 700 Bar were evaluated. For a 4% (w/w)  $\text{Na}^+$ -montmorillonite suspension flocculated with NaCl, the yield stress and plastic viscosity increased with temperature; and the plastic viscosity increased slightly with pressure. These effects were described as follows: When the particles are flocculated, higher temperatures disperse the thicker particles which causes both the yield stress and plastic viscosity to increase. Increasing the pressure was expected to increase the plastic viscosity and the yield stress slightly, due to the compression of the suspending medium. The pressure effect on the plastic viscosity was as expected; but there was a considerable reduction of the yield stress. This reduction was explained in terms of the diminution of the hydration shell of the clay particles, the latter being responsible for structure formation by mutual interaction of the extended hydration shells [cxxxvi].

Annis [cxxxvii] studied the effect of temperature on Bentonite suspensions and found that the flow curves became more non-Newtonian and shear-thinning as the temperature increased (up to  $150^\circ\text{C}$ ), displaying higher yield stresses and lower plastic viscosities. The plastic viscosity was found to decrease at the same rate as the viscosity of water. The gel strength was also determined and showed a similar trend to that of the yield stress. Namely, the change was indicative of a flocculation process of the clay suspension and was found to increase with time at high temperatures. The exposure to high temperatures for long times caused the Bentonite to become more dispersed, increasing the number of individual platelets in the suspension and increasing the viscosities at low shear rates. Addition of NaCl to the Bentonite suspension at  $100^\circ\text{C}$  severely flocculated the sample, showing stresses of a much higher magnitude compared to the Bentonite suspension alone.



Alderman et al. [cxxxviii] carried out high pressure - high temperature (HPHT) rheological measurements on water based drilling fluids containing  $\text{Na}^+$ -montmorillonite clay using a Haake Searle type viscometer. This equipment was capable of achieving temperatures up to  $150^\circ\text{C}$  and pressures up to 1000 Bar. The experimental data obtained from the flow curves were best fitted by the Herschel-Bulkley equation (eq. 5). The high shear viscosity was found to decrease with temperature and increase with pressure, being largely governed by the viscosity and compressibility characteristics of the continuous phase. The yield stress was independent of pressure and depended only weakly on the temperature, reaching a characteristic temperature ( $60^\circ\text{C}$ ) after which it increased exponentially. The onset of flocculation with temperature was suggested to be due to modification of the electrical double layer surrounding the platelets due to release of the ions, or changes in dielectrical parameters. A physically based engineering model was developed to represent the high temperature-high pressure rheological behaviour, showing good agreement with experimental data.

Briscoe et al. [cxxxix] conducted HPHT rheological measurements for concentrated Bentonite suspensions (7 - 10% w/w) using a novel HPHT rolling-ball rheometer, allowing pressures as high as 1400 Bar and temperatures up to  $140^\circ\text{C}$  to be studied. At room temperature, the yield stress was independent of the applied pressure, whereas the normalised plastic viscosity exhibited higher values as the pressure was increased. The latter effect was explained as an effective increase of the solid content due to the volume change of the liquid phase under pressure. At higher temperatures the Bentonite suspension was "thickened" and the yield stress increased with pressure. Thus the sensitivity of the pressure effect on the gelation of the clay suspensions was temperature dependent. On the other hand, the measured values for the plastic viscosity decreased significantly at the higher temperatures, but showed little variation with pressure. Heating up the Bentonite suspension increased the conductivity of the system, which indicated that more cations ( $\text{Na}^+$ ) were dissolved from the surface of the particles. It was suggested that this effect was responsible for the reduction of the normalised plastic viscosity and the observed increase of the yield stress, the latter also due to thermal induced swelling. In conclusion, volume changes in the continuous phase by hydrostatic compression or thermal expansion of the liquid phase, or modification of the electrochemical interactions between the particles was found to have a profound effect on the particle-particle interactions. An extended induced volume change model was proposed to describe the variation of the Bingham parameters of the concentrated suspensions as a function of temperature, pressure and clay content.

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