



## Effect of chemical and geometrical parameters influencing the wettability of smectite clay films



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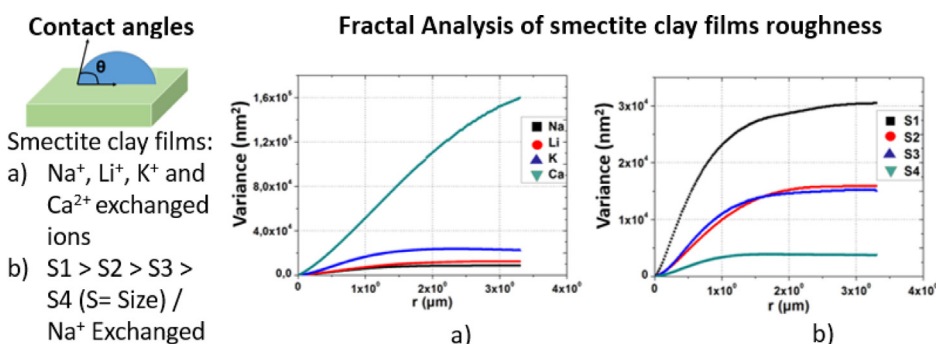
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### HIGHLIGHTS

- The influence of exchangeable ions and size of particles on the wettability of clay films is presented.
- In addition to Atomic Force Microscopy parameters, spatial correlation method used to determine the Hurst exponent and the spatial extension of roughness.
- The nature of exchangeable cation influences the roughness of the clay films but it is the hydration energies of the respective cations that *mainly* control contact angle values.
- For a given exchangeable cation, the size of clay particles influences surface roughness of films and hence contact angles.
- Wettability of clays due to surface ions: efficiency of low salinity water-flooding.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The wettability of three swelling clays (beidellite, nontronite and montmorillonite) exchanged with different interlayer ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>) was investigated by using the static sessile drop method for contact angle measurements. The results show that water contact angles on clay films vary as a function of the nature of the ion with a specific behaviour of K<sup>+</sup>-exchanged clays. The effect of various parameters influencing contact angle measurements such as relative humidity (RH), particle size and surface roughness has also been examined. RH has only a limited effect on contact angles even if drop stabilisation was observed. As far as the effect of particle size is concerned, the results obtained on montmorillonite of four different sizes show that the smallest angles are obtained on films of particles of the smallest sizes for a given exchangeable ion. This is clearly linked to differences in roughness that were deduced by analysing Atomic Force Microscopy experiments. In contrast, the nature of the exchangeable cation influences roughness in the order Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Ca<sup>2+</sup> but this order does not correspond to that deduced from the evolution of contact angles, which confirms the influence of the nature of the cation on wettability.

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## 1. Introduction

Wettability is a ubiquitous phenomenon which has attracted much attention and hence led to many publications in the field of chemistry, biology and physics. Basically, wetting is the ability of a liquid to spread, to different extents, on solid surfaces. This ability to spread, is governed by the balance of surface and interfacial forces [1]. Practically, the phenomenon of wettability is exploited in agriculture when sprays are applied to leaves or stalks for a particular treatment, in the textile industry for rain-proofing or providing fire resistance to fibres to cite few examples. Wettability is also of prime importance in the oil industry as the relative oil and water wettability governs the displacement of fluids in reservoirs [2–5]. In that context, it was shown that flooding sandstone reservoirs with low salinity water could result in additional oil yield [6–8]. However, the mechanisms associated with this technique are not fully understood and all those postulated in the literature are still prone to debate [9]. Most likely, the explanation for additional oil recovery is linked to wettability modifications in sandstone reservoirs. As such, oil is present in the pores of rocks and the injection of low salinity water is believed to displace the oil adsorbed on the walls towards the production wells as a result of wettability modifications. Most literature data converge towards the fact that the presence of clay minerals in the reservoir rock is of prime importance for LSW to be efficient. Understanding clay wettability and its dependence on various parameters is thus of prime importance for a better assessment of this new enhanced oil recovery (EOR) technique.

The present study focuses on clay samples from the smectite group, i.e. beidellite, montmorillonite and nontronite. Though such samples are not the most commonly encountered in reservoirs, they can play a significant role and are also appropriate model minerals for analysing the influence of various physico-chemical parameters. Most clay minerals possess a net charge resulting from the combination of pH dependent charges and of permanent structural charges. The pH dependent charges originate from the dangling bonds of silicate groups and the protonation or dissociation of silanols on the clays edges [10]. The role they play in the present study should however be rather marginal. The studied 2:1 smectites (two tetrahedral layers sandwiching an octahedral one), are known to possess surface charges which occur on basal surfaces of the tetrahedral sheets. As far as the permanent structural charges are concerned, they differ from each other by the location of the isomorphous substitutions. Charge deficiency in montmorillonites arises from isomorphous substitutions of  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$  in the octahedral sheets whereas for beidellites and nontronites layer charges are located in the tetrahedral sheets due to substitutions of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , respectively [11]. Due to these substitutions the platelets are negatively charged, and the resulting negative charge is compensated by exchangeable interlayer cations. It is then interesting and challenging to analyse the role of cation nature on wettability.

Wettability is commonly assessed by contact angle measurements. When possible, i.e. for smooth and non-porous surfaces, the Static Sessile Drop (SSD) method is well adapted and relatively easy to use. In this technique, a drop of the probed liquid is deposited on the substrate and the contact angle is defined as an equilibrium of the triple phase contact line. In the case of clay materials as those analysed in the present study, this method is more prone to difficulties and the results can strongly vary depending on various parameters such as nature of the surface ions [12,13], relative humidity [13,14], particle size [15,16] and surface roughness [17–21]

As far as the effect of cations nature is concerned, a few studies investigated their influence on wettability. In the case of kaolinite, a non-swelling clay mineral with exchangeable surface ions,

Biaepiotrowicz et al. [12] measured the contact angles of water and diiodomethane on surfaces with  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Al}^{3+}$  counterions. In terms of surface free energy of the different kaolinite samples, their results revealed no major difference of the dispersive components (Van der Waals type force). In contrast, the non-dispersive components (dipole-dipole, dipole-induced dipole, hydrogen bonding type forces) increased linearly on clays exchanged with  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ . A linear correlation was thus found between the non-dispersive forces and the respective entropy of hydration of the ions. Both the  $\text{K}^+$  and  $\text{Ba}^{2+}$  samples did not follow the obtained linear relationship, which was assigned to the large size of these two ions compared to the other ones. In contrast to these results, Shang et al. [13] observed negligible effect of the nature of surface ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) on water contact angles measured on samples of smectites, kaolinite and illite.

Relative humidity, RH, is an important parameter to be taken into consideration during contact angle measurements. In the interfoliar spacing of smectite clays, water molecules are associated with the interlayer cations. The interaction mechanisms of water molecules with swelling clays can be described according to two main processes [22–24]. At high water content osmotic swelling occurs for smectites with monovalent cations such as  $\text{Li}^+$  or  $\text{Na}^+$  leading to a complete exfoliation of the structure [23,24]. At lower RH, the hydration capacity of smectites mainly depends on the nature of the interlayer cation [14,25,26]. Cases et al. and Berend et al. [14,25] analysed montmorillonite swelling for various interlayer cations and observed an increase in basal spacing with hydration energy according to the following series:  $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$ . Consequently the most hydrated clays (hence with the proper exchangeable cations) are expected to give the lowest water contact angles. Concerning contact angles, Shang et al. [13] investigated the effect of relative humidities of 19, 33, 75 and 100% on smectite, kaolinite and illite with  $\text{Ca}^{2+}$  as exchangeable cation. Overall, they did not observe any general trend of the contact angles of water and diiodomethane as a function of RH at 33 and 75% but at 100% RH they recorded a decrease of the contact angles of water and an increase of that of diiodomethane.

The effect of particle size on wettability has to our knowledge not been investigated in the case of clay minerals. Data on the effect of particle size are available for other materials. For instance, Synystka et al. [15] measured dynamic contact angles on hexagonally packed silicon particles of different sizes (containing grafted polymers) and observed that increasing vertical roughness did not modify the advancing angles for particles sizes ranging from 0.2 to 10  $\mu\text{m}$ . However, the receding contact angles increased until the particles size reached 5  $\mu\text{m}$  and then decreased. In their investigations, Yang et al. determined contact angles of molybdenite powders of various sizes by Washburn's method and found that smaller particles exhibited smaller contact angles [16].

Surface roughness is a key parameter influencing contact angle measurements. When a liquid is dropped on a rugged surface, the triple phase contact line is unable to stabilise to a minimum energy [27]. Wenzel, Cassie and Baxter have described models relating contact angles to the roughness of surfaces [28,29]. Wenzel on his side described the homogeneous wetting regime and stated that upon addition of roughness on a surface, its wettability is enhanced and driven by the chemistry of the surface. For instance, a chemically hydrophobic surface becomes even more hydrophobic provided that the liquid penetrates into the grooves and that the size of the droplet is two to three times larger in magnitude than the roughness. On their side, Cassie and Baxter described the heterogeneous wetting regime where drops bridge across surface protrusions and do not penetrate into the grooves. Whether drops penetrate in grooves (homogeneous wetting regime: Wenzel model) or not

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