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**HYDRATION SEQUENCE of SWELLING CLAYS EXCHANGED with MIXED ALKALI/ALKALI-EARTH CATIONS**

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**Introduction and Principle**

Swelling clays can adsorb/adsorb a great quantity of water inside the interlayer space and the mesoporosity. This adsorbed quantity of water is strongly dependent on the nature of the interlayer cation. In order to probe the hydration sequence in clays as a function of the relative humidity (RH), XRD measurements, water adsorption and calorimetry, thermoporometry and electrical conductivity results are coupled with electrostatic calculations.

**Aim of this study :**

(i) determination of the hydration sequence of swelling clays as a function of the nature of the interlayer cations

(ii) To elucidate the mobility process of the interlayer cations as a function of the hydration state

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**Material and Method**

**Experiments**

Purified and exchanged powders of montmorillonites (Mont) from the MX80 bentonite (octahedral substitutions - saturated with a large majority of Na as interlayer cations)


Conductivity is measured in the frequency range (10⁶ Hz – 10⁷ Hz) at different temperatures (200°C-50°C for dry state and -120°C-20°C for hydrated state) with a Novocontrol impedancemeter

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**Results and Interpretation**

**Hydration Sequence**

- **Osmotic swelling in mesopores**
  - Free water is observed in mesopores only starting at RH > 90% in Li- and Na-montmorillonites

- **Sequence of hydration is depending on the interlayer cation nature**
  - Interlayer space is never completely filled by water at RH<97% for all samples except Cs+ montmorillonite

- **Diffusion coefficients at 20°C**

\[
D = \frac{\sigma kT}{(z^2 e^2 c)}
\]

\(D\) is the diffusion coefficient
\(\sigma\) is the conductivity
\(k\) the Boltzmann constant & \(T\) the temperature
\(z\) the charge of the species & \(e\) the electrical charge
\(c\) the concentration of the species
The concentration of cations is estimated from the specific surface areas calculated from water adsorption isotherm

Comparison between evolution of adsorption from X-ray diffraction (see Ferrage et al., 2005) and evolution of the diffusion coefficients

**Evolution of the mobility is impacted by both the interlayer space opening and the hydration status of the extra-framework cation**

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**Conclusion**

- **Sequence of hydration is depending on the interlayer cation nature.**
- **High mobility/diffusion of the smaller cations confirms the weak interactions existing between the hydrated Li⁺ and Na⁺ compared to the others cations.**
- **In the case of the mixture Na/Ca cations → Ca⁺⁺ is hydrated at lower RH than the Na⁺ cation as confirmed by adsorption calorimetry**