

DIELECTRIC PROPERTIES OF MONTMORILLONITES SATURATED BY BIVALENT CATIONS

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Abstract—This study deals with the analysis of dielectric measurements made on montmorillonites saturated by bivalent cations. These measurements are performed between -150°C and $+30^{\circ}\text{C}$ at frequencies ranging from 300 to 10,000 Hz. Their interpretation is based on a numerical analysis allowing determination of the dielectric losses due to free charge carriers conductivity phenomena and losses due to relaxation phenomena. The free charge carriers conductivity is due to the movement of protons. It depends very much on the nature of compensating cations and on the water content and seems to be closely related to the characteristics of the swelling.

Two types of relaxation phenomenon are described: a Debye relaxation due to electric dipole rotations and a Maxwell–Wagner relaxation due to heterogeneity effects. The analysis of the first phenomenon leads to the examination of the values of the relaxation time. It appears that the rotations of water molecules are difficult with bivalent cations. This essentially is shown by the high activation energy of the phenomenon. The discussion of these parameters shows that the state of adsorbed water molecules are certainly different as compared to the state of water molecules in ice or in liquid water. The characteristics of the second relaxation phenomenon are closely dependent on the free carriers charge conductivity.

Among the physico-chemical methods used in clay mineral studies, dielectric measurements offer many possibilities for obtaining information about the surface properties of layer-silicates. Dielectric measurements have been especially useful in the analysis of some characteristics of adsorbed water on montmorillonite (Fripiat *et al.*, 1965; Weiler and Chaussidon, 1968; Mamy, 1968).

In an alternating electric field, a clay sample is characterized by a complex dielectric constant: $\epsilon^* = \epsilon' - j\epsilon''$, where ϵ' is the real dielectric constant of the material and ϵ'' is the loss factor. This last term is proportional to the energy dissipated in the dielectric medium (Bottcher, 1952), and is made up of several components due to conductivity and relaxation phenomena. As a consequence, the results of the measurements cannot be directly interpreted, and the experimental curves $\log(\epsilon'') = f$ (reciprocal temperature) have to be numerically decomposed into different parts corresponding to the conductivity and relaxation phenomena.

EXPERIMENTAL RESULTS

The clay used is the montmorillonite of Camp Beateau, the formula of which is



The measured exchange capacity is 116 m-equiv./100 g of clay dried at 1000°C .

Dielectric properties were determined on clay samples made of pressed powder (30 kg/cm²). These sam-

ples were equilibrated over sulfuric acid solutions in order to fix their water content. The measurements were made between -150°C and $+30^{\circ}\text{C}$ for the frequencies: 300, 500, 1000, 2000, 5000 and 10,000 Hz. The technological details of the cell used have been published by Mamy (1968). The apparatus consists of a generator Wayne-Kerr S 121, an electrical bridge Wayne-Kerr B 221 and a wave analyser Wayne-Kerr A 321.

The experimental results are represented by two sets of curves: $\log \epsilon'' = f(1/T)$ and $\tan \delta = \epsilon''/\epsilon' = f'(T)$. Such curves are obtained for each cation (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) at one frequency, for a given water content (it will be always expressed in g water/100 g of clay dried at 250°C). The variation of $\log \epsilon''$ are given in Fig. 1.

In previous work (Calvet, 1972 a) we have shown that it was possible to describe two conductivity phenomena for montmorillonites saturated by monovalent cations (Mamy, 1968). One of these conductivities is dominant at low temperatures ($< -100^{\circ}\text{C}$) and is designated by σ_1 , the other is dominant at high temperatures and is designated by σ_2 . The corresponding dielectric losses are ϵ''_1 and ϵ''_2 . We have also described two absorption phenomena. The first, is weak and can be attributed to a Debye relaxation ($\epsilon''_d =$ dielectric loss), the second, much stronger is only visible for water contents greater than 9.5% and is due to a Maxwell–Wagner relaxation (dielectric loss = ϵ''_w). Thus, the total dielectric loss ϵ'' is:

$$\epsilon'' = \epsilon''_1 + \epsilon''_2 + \epsilon''_d + \epsilon''_w. \quad (1)$$

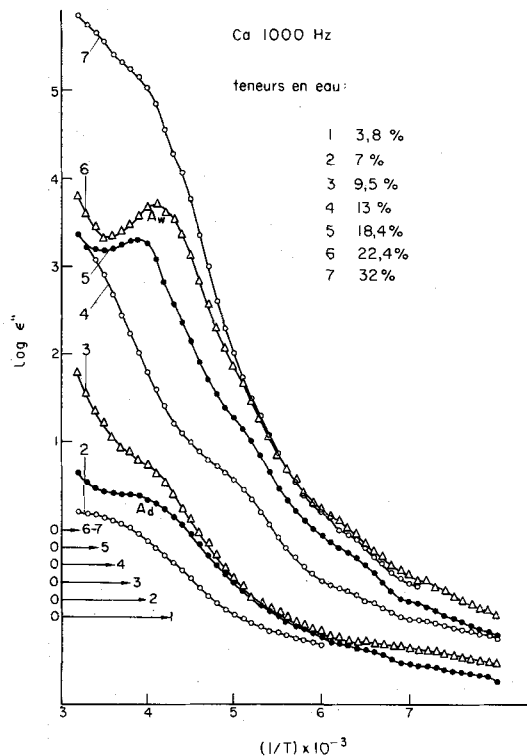


Fig. 1a

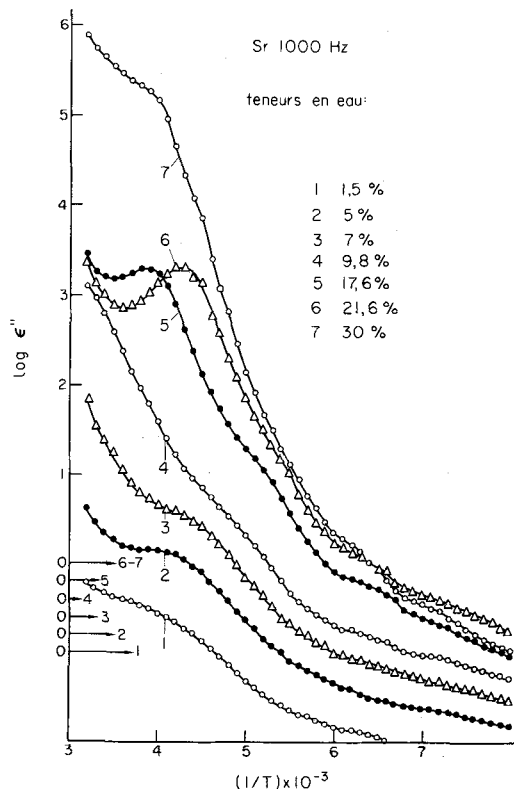


Fig. 1b

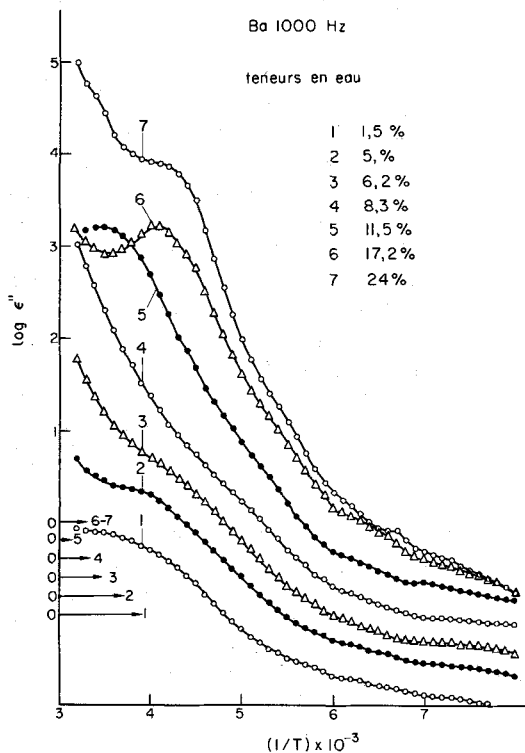


Fig. 1c

Fig. 1. Variations of the logarithm of the total dielectric loss against the reciprocal temperature. For each curve, the scale of $\log \epsilon''$ is shifted in order to avoid overlaps of the curves.

Using a numerical method, it is possible to obtain the values of the parameters which determine ϵ''_1 , ϵ''_2 , ϵ''_d and ϵ''_w . These values are adjusted in order to obtain the best fit between the curves representing $\log(\epsilon''$ experimental) and $\log(\epsilon''$ calculated).

Figure 2 shows two examples of decomposition of the curves $\log \epsilon''$ selected so as to represent the main types of experimental curves (from Calvet, 1972 a).

Conductivity phenomena

We have observed that the values of σ_2 decrease when the frequency of the applied electric field increases. Thus, we can say that σ_2 is really due to the displacement of charge carriers (Freymann and Freymann, 1954).

The relation between the conductivity and the temperature is given by the Arrhenius law:

$$\begin{aligned} \sigma_1 &= \sigma_{01} \exp(-W_1/RT) \\ \sigma_2 &= \sigma_{02} \exp(-W_2/RT) \end{aligned}$$

σ_1 and σ_2 are calculated from the values of the corresponding dielectric losses:

$$\begin{aligned} \epsilon''_1 &= Co_1 \exp(-W_1/RT), & Co_1 &= \sigma_{01}/2\pi\nu\kappa_0 \\ \epsilon''_2 &= Co_2 \exp(-W_2/RT), & Co_2 &= \sigma_{02}/2\pi\nu\kappa_0 \end{aligned} \quad (2)$$

where ν is the frequency and κ_0 the vacuum permittivity. The constants Co_1 , Co_2 and the activation energies W_1 and W_2 are given by the numerical calculation.

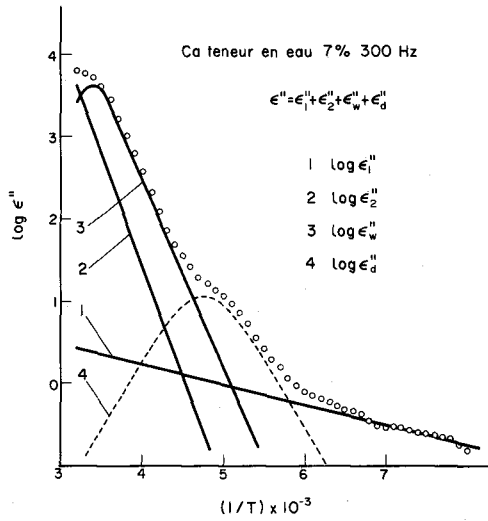


Fig. 2a

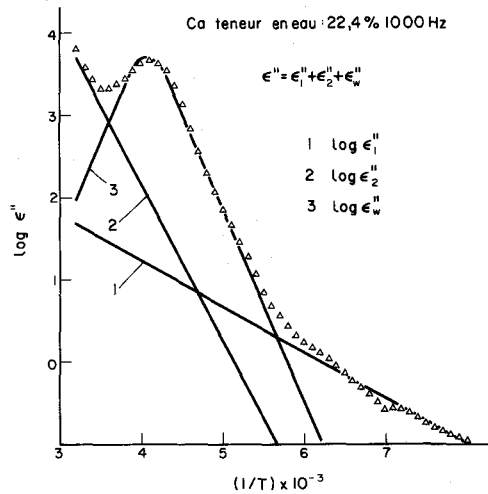


Fig. 2b

Fig. 2. Results of the numerical analysis of the curve $\log \epsilon'' = f(1/T)$. (Calvet, 1972a).

At temperatures below -100°C , the dominant conductivity σ_1 is essentially characterized by a low activation energy (1–3 kcal/mole) probably due to the migration of protons by tunnel effect. However, the most interesting results are those of the other conductivity phenomenon σ_2 which we shall examine in some detail. Figure 3 represents the variations of $\log \sigma_2$ as a function of the clay water content at 20°C for 1000 Hz.

It appears that the conductivity of the hydrated mineral depends on the nature of the exchangeable cation and is much greater for the sodium-clay (for this clay, the results are taken from Mamy, 1968). It also depends on the water content which determines both the nature of the influence of the cation and the intensity of the phenomenon. With the con-

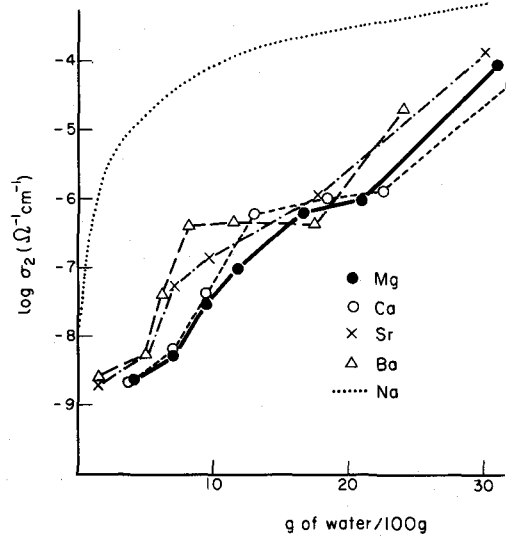


Fig. 3. Variations of the conductivity with the water content.

ductivity values as a basis, three domains of water content can roughly be defined:

- (1) $<13\text{--}14\%$: $\sigma_{\text{Ba}} > \sigma_{\text{Sr}} > \sigma_{\text{Ca}} > \sigma_{\text{Mg}}$
- (2) $(13\text{--}14\%)$ to 20% : $\sigma_{\text{Ba}} \approx \sigma_{\text{Sr}} \approx \sigma_{\text{Ca}} \approx \sigma_{\text{Mg}}$, and
- (3) $<20\%$: $\sigma_{\text{Ba}} \approx \sigma_{\text{Sr}} > \sigma_{\text{Mg}} > \sigma_{\text{Ca}}$.

It is interesting to compare the conductivity variations with those of the 001 spacings of the clays which are given in Fig. 4 (from Calvet, 1972 b). First, we note that when the water content is less than 14% , the values of 001 augment in the order $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$ which is the inverse of the conductivity order. A low 001 value is thus associated with a high conductivity for these hydration states. We can see also that an important increase of the 001 spacing is not always accompanied by a great increase of the conductivity which can be constant as in the case of the Ba-clay. Another observation deals with the clay at water contents greater than 20% for which the increase of 001 spacing is

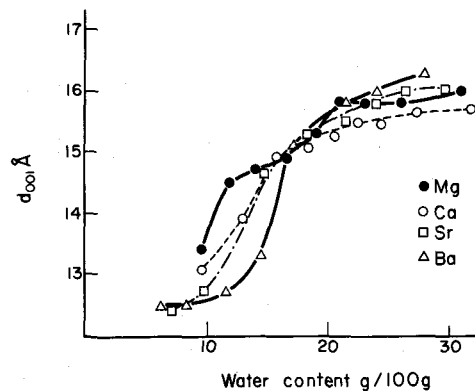


Fig. 4. Apparent spacing d_{001} for different water contents.

Table 1. Activation energy of the conductivity phenomenon

Cation	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
Water content g/100 g	7	7	7	6.2
W ₂ .k cal mole ⁻¹	5.8	7	9.3	8.2
Water content g/100 g	16.4	18.4	17.6	17.2
W ₂ . cal mole ⁻¹	9.8	9	9.4	6
Water content g/100 g	20.9	22.4	21.6	
W ₂ .k cal mole ⁻¹	10	9.2	8.4	

small even though the conductivity increases very much.

The activation energy of the conductivity σ_2 is higher than that of the conductivity σ_1 . Some values obtained by the numerical adjustment are given in Table 1.

Relaxation phenomena

Debye relaxation phenomenon. The dielectric loss ϵ''_d and the tangent of the loss angle δ_d are given by the following expressions (Cole, 1941):

$$\epsilon''_d = \eta_d \cdot \frac{\sin(\eta\pi/2)(\omega\tau_d)^n}{1 + 2 \cos(\eta\pi/2)(\omega\tau_d)^n + (\omega\tau_d)^{2n}} \tag{3}$$

$$tg \delta_d = \frac{\epsilon''_d}{\epsilon'_d} = \frac{(Q - 1) \sin(\eta\pi/2) \cdot (\omega\tau_d)^n}{Q + (Q + 1) \cos(\eta\pi/2) \cdot (\omega\tau_d)^n + (\omega\tau_d)^{2n}} \tag{4}$$

where:

ϵ'_d = real dielectric constant
 $\eta_d = \epsilon_0 - \epsilon_\infty$ and $Q = \epsilon_0/\epsilon_\infty$; ϵ_0 and ϵ_∞ being respectively the static and high frequency dielectric constant.

Table 2. Numerical values of η_d

Frequency	300	1000	300	1000	300	1000	300	1000
Mg ²⁺	% water		4	7	9.5		11.8	
	η_d	51.8 21.5	47.5 39.3	47.8 39	21.8	20.8		
Ca ²⁺	% water		3.8	7	9.5		13	
	η_d	72.2 62	93.4 69.8	151.4 117	87.6	61.8		
Sr ²⁺	% water		1.5	5	7		9.8	
	η_d	13.2 9.3	41.1 40.9	65.1 68.4	38.8	17.5		
Ba ²⁺	% water		1.5	5	6.2		8.3	
	η_d	32.3 16.3	90.2 79.3	90 94	—	—		

Table 3. Values of T_{dm} , T'_dm and Δ_d for Ca-montmorillonite at a water content of 7%.

Frequency HZ	T_{dm} °K	T'_dm °K	$\Delta_d \times 10^3$
300	248	229	0.337
500	251	232	0.332
1000	257	237	0.326
2000	261	242	0.299
5000	269	248	0.318
10,000	276	255	0.298

τ_d = relaxation time. In terms of the theory of rate processes, it is expressed as (Gladstone *et al.*, 1941):

$$\tau_d = \frac{h}{kT} \cdot \exp\left(-\frac{\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right) = \tau_{0d} \exp\left(\frac{\beta_d}{T}\right) \tag{5}$$

with ΔS and ΔH representing the entropy and enthalpy of activation.

n = parameter which describes the spread of the relaxation time

T = absolute temperature

h = Planck constant

k = Boltzman constant

R = molecular gas constant

$\omega = 2\pi\nu$; ν = frequency.

The parameters η_d , β_d , τ_{0d} and n are obtained by the numerical calculation.

Numerical values of ϵ_0 and ϵ_∞ are calculated from η_d and Q . Table 2 gives some values of η_d corresponding to the maximum of ϵ''_d , at two frequencies and for different water contents. Since T_{dm} , the temperature of the maximum of ϵ''_d , increases as the frequency increases, Table 2 shows that the value of η_d is a decreasing function of the temperature. This is illustrated by Fig. 5 where η_d is plotted against $1/T_{dm}$. It appears that we have a relation of the type

$$\eta_d = \eta_0 + \frac{K}{T} = \epsilon_0 - \epsilon_\infty \tag{6}$$

with η_0 and K = constants.

This relation is at least valuable for temperatures not too far from the domain where the maxima of ϵ''_d are observed.

The ratio $Q = \epsilon_0/\epsilon_\infty$ is calculated from the relation

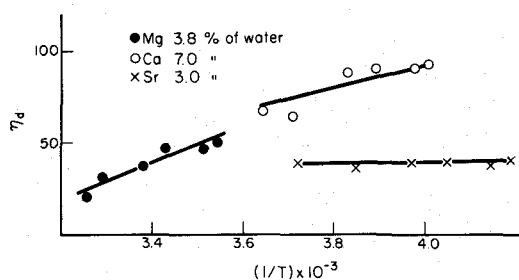
$$\frac{\partial}{\partial(1/T)} (tg \delta_d) = 0$$

which occurs for $T = T'_dm$, the temperature of the maximum of $tg \delta_d$. In doing this calculation we have taken

$$\frac{d}{d(1/T)} (\epsilon_\infty) = 0$$

(Eisenberg and Kauzmann, 1970; Kelly and Salomon, 1969).

Furthermore, it is interesting to note that the analytical expression of T_{dm} obtained by using (4) leads

Fig. 5. Variations of η_d against $1/T$.

to the following relation:

$$\frac{1}{T_d m} = \frac{1}{\eta \beta_d} L_n G + \frac{1}{T_d m} \quad (7)$$

where G is a function of K , η_d , Q , n and β_d . This formula has two consequences:

- (1) we have always $T_d m < T_d m$.
- (2) the difference

$$\Delta = \frac{1}{T_d m} - \frac{1}{T_d m}$$

decreases as the frequency ν increases since it can be shown that G is a decreasing function of ν . Table 3 gives the values of $T_d m$ derived from the numerical adjustment and of $T_d m$ directly obtained from the experimental curves of $\log \delta$. It appears that the previous deductions from (7) are verified, which confirms the validity of the calculation used in this work.

A small error on $T_d m$ leads to a great error on the value of Q . Thus, although the temperatures $T_d m$ are correct, it is not possible to calculate the exact values of ϵ_0 and ϵ_∞ . We can only give approximations which for montmorillonites saturated by bivalent cations are:

$$\epsilon_x \approx 10 \quad \text{and} \quad \epsilon_0 \approx 50-100 \quad (\text{at } 250 \text{ K})$$

In terms of the theory of rate processes the relaxation time τ_d is described by the relation (5). The entropy of activation ΔS is always positive and its absolute value is about 30 cal/mole/degree. This means that the polarization increases very much the ordering of the dipoles through an important molecular rearrangement. Table 4 contains several values of the enthalpy of activation ΔH . Examples of τ_d values are given in Table 5.

Table 4. Values of the enthalpy ΔH of the Debye relaxation phenomenon

Mg^{2+}	Water content	4	7	9.5	11.8
	ΔH k cal mole ⁻¹	23.4 ± 1.2	22.2 ± 1.2	19.2 ± 1.6	17.2 ± 1.4
Ca^{2+}	Water content	3.8	7	9.5	13
	ΔH k cal mole ⁻¹	20 ± 3	19.8 ± 1.4	23 ± 2.6	25 ± 2.8
Sr^{2+}	Water content	1.5	5	7	9.8
	ΔH k cal mole ⁻¹	18.8 ± 0.8	14.8 ± 0.8	16 ± 1.1	21 ± 3.6
Ba^{2+}	Water content	1.5	5	6.2	8.3
	ΔH k cal mole ⁻¹	17.8 ± 1.5	17.2 ± 1.4	12.6 ± 1.1	10.8 ± 2.2

Table 5. Values of the relaxation time τ_d

Cation	Water content g/100 g	$T = 263^\circ\text{K}$		$T = 293^\circ\text{K}$	
		τ_d	Ice*	τ_d	liquid* water
Mg^{2+}	7	$7.6 \cdot 10^{-4}$		$9.5 \cdot 10^{-6}$	
Ca^{2+}	7	$5.5 \cdot 10^{-5}$	$3.8 \cdot 10^{-6}$	$1.1 \cdot 10^{-7}$	$9.6 \cdot 10^{-12}$
Sr^{2+}	7	$7.4 \cdot 10^{-6}$		$3.2 \cdot 10^{-7}$	
Ba^{2+}	6.2	$1.8 \cdot 10^{-4}$		$1.6 \cdot 10^{-5}$	

* These values are taken from Eisenberg and Kauzmann (1969).

Maxwell-Wagner relaxation phenomenon. This relaxation phenomenon is characterized by the following features; (a) the corresponding absorption is intense and is revealed by a high maximum value both on the $\log \epsilon'' = f(1/T)$ and $\log \delta = f(T)$ curves (the maximum value of ϵ''_w is frequently higher than 1000), (b) it is only visible in systems with a water content higher than 10–13%, (c) for a given water content the maximum of absorption shifts towards the high temperatures when the frequency increases. For a given frequency it shifts towards the low temperatures as the water content increases.

This phenomenon can be due either to an heterogeneity of the aggregates or to the heterogeneity of aggregate arrangements. We are concerned with clay samples as mixtures of a conducting medium, the water in all its different forms, and of an insulating material, the silicate layers. In order to describe the electric properties of such a system, we have used the theory of the Maxwell-Wagner effect in the form proposed by Sillars (1937). This theory is based on a model in which the conducting medium made of ellipsoidal particles, is dispersed in the insulating material. Since it is supposed that the particle dimensions are small as compared to the distances between them, the foreseen electrical effects may be underestimated (Sillars, 1937). In this theory, the dielectric loss of the heterogeneous material is given by:

$$\epsilon''_w = q \epsilon_2'' \frac{L^2 \epsilon_1'^2}{[\epsilon_1'(L-1) + \epsilon_2']^2 + \epsilon_2''^2}, \quad (8)$$

where

ϵ_1' = dielectric constant of the silicate layers. We have supposed during this work that it is independent of the temperature

ϵ'_2 = dielectric constant of the conducting medium
 ϵ''_2 = dielectric loss due to the conductivity phenomenon

q = volume proportion of the conducting medium

L = function of the axis dimensions of the ellipsoidal conducting particle. When $L > 1$ we have an elongated particle.

The relation (8) can be written as:

$$\epsilon''_w = \eta_w \frac{\omega\tau_w}{1 + \omega^2\tau_w^2} \quad (9)$$

with:

$$\eta_w = q \frac{L^2\epsilon'_1{}^3}{\epsilon'_1(L-1) + \epsilon'_2}$$

$$\omega\tau_w = \frac{\epsilon'_1(L-1) + \epsilon'_2}{\epsilon''_2} \quad (10)$$

$$\omega\tau_w = \omega\tau_{0w} \exp(\beta_w/T)$$

$\beta_w = \Delta H_w/R$, ΔH_w being the activation energy associated to the relaxation phenomenon. The formulas (9) and (10) are used in the numerical adjustment. The values of β_w and that of the activation energy W_2 of the conductivity σ_2 are related by:

$$W_2 = R\beta_w \quad (11)$$

(This can be shown from formulas (2) and (9)).

Values of W_2 and $R\beta_w$ obtained by the adjustment are given in Table 6. Since they are with an error of about 10% we see that the equality (11) is rather well verified. We can thus conclude that the studied relaxation phenomenon is really due to a Maxwell-Wagner effect.

DISCUSSION

It has been shown that the conductivity of a hydrated clay without free salts is due to the migration of the protons (Fripiat *et al.*, 1965; Calvet and Mamy, 1971). As a consequence, the characteristics of this conductivity phenomenon must be closely related to the properties of adsorbed water.

Before discussing the results obtained for the conductivity σ_2 , it is interesting to make some comments on the swelling of montmorillonites saturated by bivalent cations. The first hydration step for these minerals is probably the formation of hexahydrates

Table 6. Comparison between the values of W_2 and $R\beta_w$

	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
Water content g/100 g	16.4	18.4	17.6	6.2
W_2 k cal mole ⁻¹	9.8	9	9.4	8.2
$R\beta_w$ k cal mole ⁻¹	9.9	10.7	10.7	9.3
Water content g/100 g	20.9	22.4	21.6	
W_2 k cal mole ⁻¹	10	9.2	8.4	
$R\beta_w$ k cal mole ⁻¹	12.7	10.6	9.8	

of the compensating cations (Glaeser, 1953). This brings about an expansion of the silicate layers which leads to an interlamellar spacing of approximately two molecular diameters of water. Then, as the hydration increases, a fraction of the newly adsorbed molecules occupies the space left by the hydrated cations on the accessible internal surface and on the external surface. Let us call the molecules of this fraction, the 'filling' molecules. So, two layers can be separated without interlayer spaces being completely filled. Figure 4 shows that the swelling is greatly influenced by the nature of the cations. For a given water content below 20%, the swelling increases in the order: Ba²⁺ < Sr²⁺ < Ca²⁺ < Mg²⁺. Thus, it is probable that the number of "filling" molecules follows the inverse order, being greater with Ba²⁺. Moreover, when the water content is raised, one can think that a great variation of d_{001} must be associated to small or no increase of the number of the 'filling' molecules, and on the contrary, a small variation of d_{001} must be associated to a great increase of the amount of these molecules.

When we consider the values of the conductivity σ_2 and the characteristics of the swelling just discussed, we are led to conclude that a high value of σ_2 is probably due to the presence of a large number of 'filling' molecules. Under these conditions we can write the following relations shown in Table 7.

Figure 3 shows that Na-montmorillonite has a higher conductivity than the clays saturated by bivalent cations whatever the water content. This can be due to a greater ability of molecular arrangement to transfer the proton and/or to a larger number of 'filling' molecules. Thus, it appears that this kind of water molecule seems to play an important part because these molecules can be an efficient transition state for the movements of the protons, or can build

Table 7. Relations between the conductivity and the variations of the apparent spacing d_{001}

Water content g/100 g	d_{001}	Number of 'filling' molecules	Conductivity
	Low value (Ba < Sr < Ca < Mg)	(Ba > Sr > Ca > Mg)	(Ba > Sr > Ca > Mg)
< 14			
14-20	+++	+ or 0	+ or 0
> 20	+	+++	+++

0: no increase. +: small increase. +++: great increase.

up a continuous water film on the surface and ensure the interaggregate contacts. Otherwise, it has been shown that this last argument holds in the case of calcium-phlogopite (Mamy, 1972).

Although the dielectric measurements have been made at different temperatures, the preceding discussion is always valuable as long as the water content is less than 25–30%. For higher hydration states, it has been shown that the d_{001} value is modified during freezing and that ice is formed outside the clay aggregates (Anderson, 1965, 1971). This is probably the case for the clay at 30% water. However, we have not observed a transition phase on the $\log \epsilon''$ curves owing to the Maxwell–Wagner relaxation phenomenon.

It must be noted that we have no observations concerning the Debye relaxation phenomenon for water contents greater than $\approx 12\%$. This is because the corresponding ϵ_d'' values become small as compared to the other dielectric losses ϵ_2'' and ϵ_w'' . Under these conditions, it was not possible to take into account ϵ_d'' in the numerical calculation used to decompose the curve $\log \epsilon'' = f(1/T)$. So, this part of the discussion is restricted to water contents of less than $\approx 12\%$.

Compared to sodium–montmorillonite, the clays saturated by bivalent cations present high values of ϵ_∞ and ϵ_0 .

Na–montmorillonite: $\epsilon_\infty = 3.5$;

$$\epsilon_0 = 18.5 (175 \text{ K}) \text{ (Mamy, 1968)}$$

Bivalent cation: $\epsilon_\infty \approx 10$;

$$\epsilon_0 \approx 50\text{--}100 (250 \text{ K}).$$

Except possible variations of the polarizability, the observed difference could be due to the rotations and translations of water molecules (Haggis *et al.*, 1952), suggesting that the number of hydrogen bonds is greater in a hydrated Na–clay than in the montmorillonites with bivalent cations.

The theory of Kirkwood states that (Eisenberg and Kauzmann, 1969);

$$\epsilon_0 = 2\pi N^* \frac{m^2 g}{kT},$$

where

N^* = number of dipoles per unit volume

m = average dipole moment

g = Kirkwood correlation parameter.

This relation shows that ϵ_0 must decrease as the temperature increases, in agreement with the results previously given (see formula 6). Moreover, taking into account the polarizing power of monovalent and bivalent cations we can write:

$$m(\text{Ca}) > m(\text{Na}) \quad \text{and} \quad g(\text{Ca}) > g(\text{Na})$$

These inequalities can explain the difference between the observed values of ϵ_0 .

Two other points relative to the Debye relaxation phenomenon are interesting to discuss: the values of the relaxation time τ_d and the value of the activation energy. The first value allows us to get some information relative to the rotational movements of water and the displacements of protons. This can be done by comparing the mean interval between two successive associations of a given water molecule with a proton: $\tau_{\text{H}_2\text{O}}$ to the rotational correlation time τ_{rd} . For the systems studied here, τ_{rd} is of the same order of magnitude as τ_d since:

$$\tau_{rd} = \frac{3\epsilon_0 + \epsilon_\infty}{3\epsilon_0} \tau_d$$

The value of $\tau_{\text{H}_2\text{O}}$ is given by Eisenberg and Kauzmann (1969).

$$\tau_{\text{H}_2\text{O}} = \tau_{\text{H}^+} \cdot \frac{[\text{H}_2\text{O}]}{[\text{H}^+]} = \tau_{\text{H}^+} \cdot \frac{1}{\alpha}$$

where τ_{H^+} is the mean period of association of a proton with a given water molecule. Its value is roughly $10^{-12} - 10^{-13}$ s. α is the dissociation coefficient of the water molecule which we have taken equal to $10^{-3} - 10^{-4}$ for the adsorbed state (Fripiat *et al.*, 1965). Table 8 shows the comparison between clays saturated by monovalent and bivalent cations and the water or the ice.

From the values given for τ_d in Table 5 we have the order of magnitude of τ_{rd} . The figures contained in Table 8 suggest that in ice, water and also for water adsorbed on Na–montmorillonite, the water molecules experience many orientations between two successive associations with a proton, because $\tau_{rd} < \tau_{\text{H}_2\text{O}}$ for the water adsorbed on clays saturated by bivalent

Table 8. Comparison between $\tau_{\text{H}_2\text{O}}$ and τ_{rd}

	$T = 263^\circ\text{K}$			$T = 293^\circ\text{K}$		
	Clays saturated by bivalent cations	Clays saturated by monovalent cations	Ice*	Clays saturated by bivalent cations	Clays saturated by monovalent cations	Liquid water
α	$10^{-4} - 10^{-3}$	$10^{-4} - 10^{-3}$	$5.4 \cdot 10^{-14}$	$10^{-4} - 10^{-3}$	$10^{-4} - 10^{-3}$	$1.8 \cdot 10^{-9}$
$\tau_{\text{H}_2\text{O}}$	$10^{-8} - 10^{-10}$	$10^{-8} - 10^{-10}$	$1.85 - 1.85 \cdot 10^{-1}$	$10^{-8} - 10^{-10}$	$10^{-8} - 10^{-10}$	$5.5 \cdot 10^{-4} - 5.5 \cdot 10^{-5}$
τ_{rd}	$10^{-4} - 10^{-5}$	10^{-10}	$3.8 \cdot 10^{-6}$	$10^{-5} - 10^{-6}$	10^{-12}	$9.6 \cdot 10^{-12}$

* The corresponding values are taken from Eisenberg and Kauzmann (1969).

cations the water molecules do not have enough time to experience a rotation between two successive associations with a proton, because $\tau_{rd} > \tau_{H_2O}$.

The relaxation phenomenon associated with adsorbed water is characterized by a wide spread of the relaxation time (computed value of $n = 0.34$ whatever the cation). This means that there are a large number of different environments for the water molecules adsorbed on the clay surface. A similar conclusion was deduced from the analysis of the repartition of water molecules relative to the exchangeable cations (Calvet, 1973).

The values of the enthalpy of activation are relatively high except for the montmorillonite saturated by Ba^{2+} at 6.2 and 8.3% of water. We note also that with bivalent cations ΔH is always greater than with monovalent cations for which the mean value is about 10–12 kcal/mole (Mamy, 1968).

We have to remark that the activation energy ΔH of the relaxation process is greater than the activation energy of the conductivity σ_2 . This implies either that the rotations of water molecules are not a limiting factor for the conductivity or that the relaxation phenomenon must be attributed to molecules which do not participate to the conductivity phenomenon.

The second relaxation phenomenon called Maxwell–Wagner relaxation is due to the heterogeneity effects and is described by the formula (8). The samples used are made of compressed aggregates of clay and the meaning of the parameter L is not simple. We can only say that, the greater the value of L , the greater the length of the conducting pathways (the lengths are taken parallel to the electric field direction). We can think also that L should be related to the structural properties of the samples such as the porosity and the tortuosity and to the water content. However we can get some information about the part played by the parameter L . Let us consider the relation which gives the value of the temperature T_{wm} corresponding to the maximum of ϵ''_w .

$$\frac{1}{T_{wm}} = \frac{1}{w_2} L_n \left(\frac{C_{O_2}}{\epsilon'_1(L-1) + \epsilon'_2} \right) \quad (12)$$

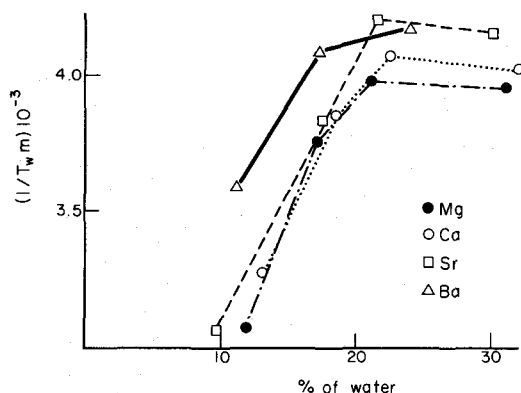


Fig. 6. Effect of the water content on the value of T_{wm} .

It appears that T_{wm} decreases as the conductivity σ_2 increases (increasing C_{O_2} , decreasing W_2). The dehydration of the clay is thus accompanied by an increase of T_{wm} since σ_2 decreases during this process. This is shown by the Fig. 6. However, a large increase of σ_2 does not lead always to an important diminution of T_{wm} . For example, at a water content of about 30%, the values of T_{wm} are not very different from those observed at 20% whereas the conductivity has increased very much. Under these conditions, the relation (12) shows that L must be greater at 30% than at 20%. We can thus relate a marked increase of L to a greater increase of σ_2 . This result confirms the preceding conclusion as to the role of 'filling' water molecules. When their number increases the conducting pathways length is raised either by the filling of the interlamellar spaces or by setting up interaggregate contacts through accumulation of water on external surface.

Generally, the interpretation of conductivity measurements made on clay samples are difficult on account of the Maxwell–Wagner relaxation phenomenon. This is due to the fact that it is not easy to separate the contribution of free charge carriers from that of the heterogeneity effect. Thus, it is interesting to evaluate the importance of this difficulty. Putting

$$A = qL^2 \epsilon_1'^2 \quad \text{and} \quad B = [\epsilon_1'(L-1) + \epsilon_2']^2$$

we have from formula (8):

$$\epsilon''_w = \frac{A\epsilon_2''}{B + \epsilon_2''^2}$$

Since the measurements are made at temperatures below 30°C, we are essentially concerned by the case $T < T_{wm}$ especially for low water contents. Under these conditions $\epsilon_2''^2 \ll B$ so that $\epsilon''_w \simeq (A/B) \epsilon_2''$. Then the total dielectric loss is:

$$\begin{aligned} \epsilon'' &= \epsilon''_w + \epsilon_2'' = \left(\frac{A}{B} + 1 \right) \epsilon_2'' \\ &= C_{O_2} \left(\frac{A}{B} + 1 \right) \exp(-W_2/RT) \end{aligned}$$

(in general, in the domain of temperature where we have to take into account ϵ''_w and ϵ_2'' , we can neglect ϵ''_d and ϵ_1'' since their values are very small. See, e.g. Fig. 2.

The analysis of the possible values of A and B shows that the ratio A/B is always less than unity. Thus, the upper limit of ϵ'' is $2\epsilon_2''$. Moreover, for low water contents (generally below 7%), we see that it is possible to get directly the correct value of the activation energy of the conductivity σ_2 from the measurements of the total dielectric loss at different temperatures. On the contrary, this is not the case for the preexponential term which is not equal to C_{O_2} .

CONCLUSION

Two kinds of conclusions may be drawn. The first concerns the method used in this work to analyse

the experimental results of dielectric measurements. Because of their complexity, these results cannot be interpreted directly and it is necessary to perform a numerical analysis in order to describe the conductivity and relaxation phenomena. In spite of the hypothesis contained in the formalism used to represent the dielectric behaviour of the clay samples and of the approximations included in the numerical calculation itself, it is possible to obtain precious informations concerning the characteristics of the conductivity and relaxation phenomena.

The second kind of conclusion is related to the large amount of information provided by the dielectric measurements. Furthermore, this information is situated at two different levels. Some concern the molecular properties of adsorbed water molecules, others are related to macroscopic properties of the clay samples, that is to say, the properties directly determined by the arrangement of the clay aggregates.

The study of the dominant conductivity phenomenon at high temperatures and of the relaxation phenomena allows us to emphasize some aspects of the clay-water relationships such as the characteristics of the swelling, the properties of adsorbed water.

It appears that the conductivity is largely determined by the 'filling' molecules, i.e. molecules which are not those of the hydration of the compensating cations. Their role probably is to allow the transfer of protons both in interlamellar spaces and between the clay aggregates. On the other hand, the results of the Debye relaxation show that the water molecules concerned by this phenomenon probably do not participate in the conductivity. We can conclude also that the dielectric properties of adsorbed water are extensively dependent on the nature of the exchangeable cations and clearly different from that of ice or liquid water, at least when the water content of the clay is less than 25–30%.

Concerning the Maxwell–Wagner relaxation, two points have to be noted; Firstly this phenomenon can probably be used to study the structure and properties of clay aggregates since its variations are closely related to the conductivity and secondly it can be also troublesome for the measurement of the conductivity due to free charge carriers. However we have shown that it is possible to neglect it for the determination of the activation energy of this process for clays with water content less than 7%.

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