

SURFACE CONDUCTIVITY AND DIELECTRICAL PROPERTIES OF MONTMORILLONITE GELS*

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Abstract—The surface conductivity of salt free montmorillonite clay gels saturated with lithium, sodium, potassium and cesium has been studied. The theory of the behavior of heterogeneous dielectrics adapted to systems having a surface charge density has been applied to the clay gels. From numerical calculations it became evident that the value of the depolarization factor may be extrapolated to 1 in the direction of the small axis of the platelet, meaning that the field action is zero in this direction. Along the long axis, however, the action is complete and the motion of the charge carriers is essentially tangential to the platelet. The values of the surface conductance are of an order of magnitude of 10^{-9} Mho.

The investigation of the behavior of the water molecules has been carried out over a wide temperature range (145–320°K). At temperatures below 273°K, the conduction appears to be predominantly protonic; the counterions are considered to be disturbing elements in the water layer structures, thus creating a number of lattice defects able to transport the current. Above 273°K, the conduction is essentially due to the adsorbed cations, their contribution starts during the phase change.

INTRODUCTION

THE BEHAVIOR of heterogeneous dielectrics has kept the attention of many investigators and the systems studied vary from clay minerals (Martin, 1962; Street, 1956; van Olphen, 1957), to glass powders (Fripiat, Jelli and Poncelet, 1965), silica gels (Young and Crowell, 1962; Freymann and Freymann, 1954), biological cells (Fricke and Curtis, 1937; Schwan, Schwarz, Maczuk and Pauly, 1962) and proteins (Oncley, 1942; Takashima and Schwan, 1965).

Maxwell (1891) was the first to give a formulation of the electrical conduction in heterogeneous media and to propose a theory of the behavior of composite dielectrics. Later Wagner (1913, 1914) extended Maxwell's formulation and stressed the importance of the frequency of the a.c. field and of the geometry of the system, and is known under the name Maxwell–Wagner-effect.

Sillars (1937) and Fricke (1924, 1953) generalized the theory to systems where the dispersed phase consists of ellipsoids.

However, these theories do not cover the rather common case in which at the interface an electric double layer exists, which gives rise to such phenomena as surface or double layer conductance.

Recently, O'Konski developed a theory which

took cognizance of the presence of a diffuse electrical double layer. We have applied his approach to clay systems. We assumed a model in which the conductance is essentially tangential to the clay platelet, and limited to a thin zone near the surface. We considered the nature of the charge carriers, the effect of hydration of the charge carriers, and the possible contribution of water molecules to the conductivity.

An investigation over a wide temperature range led us to interpret the conduction at temperatures below 273°K as essentially protonic, being a result of lattice defects in the water structure, (Freymann and Soutif, 1960; Gränicher *et al.*, 1957), while above 273°K the conductivity is due to the motion of the counterions.

EXPERIMENTAL SECTION

Materials

The experiments are carried out with a montmorillonite clay from Camp Berteau, Morocco. The fraction $<2 \mu$ is obtained through successive sedimentation of the sodium saturated clay. The pH is kept in the vicinity of neutrality. Four monovalent homoionic systems are studied with the following base exchange capacity: lithium clay, 97.5 mE/100 g; sodium clay, 98 mE/100 g; potassium clay, 98.5 mE/100 g and cesium clay, 95 mE/100 g.

All the systems investigated are salt free gels.

*Based on the dissertation submitted by R. A. Weiler for the Ph.D. degree.

Concentrations are expressed as percentages (g/100 g) of clay based on weights obtained after drying at 105°C. These vary from 10 to 60 per cent.

Apparatus

The cell consists essentially of a flat capacitor; the two electrodes are made of bronze and are circular in shape with a diameter of 1 cm. The distance between the two electrodes is variable, and is generally set from 0.25 to 0.32 cm (Von Hippel, 1961). The accuracy of this distance is known within 0.02 mm. The clay gel is located between the two electrodes and is thus the dielectric of the capacitor. This ensemble is surrounded by a teflon jacket and is located in a bronze block which ends in a 20 cm long cylinder of a diameter of 2.5 cm. The latter is immersed in liquid air for the experiments below 273°K. After 90 min a temperature of 145°K is obtained in the upper part. Once this temperature is reached, the entire system is then slowly heated up to 320°K, an operation which takes about 5 hr. The temperature in the block is measured with a thermocouple and known within a few tenths of a degree.

The components of the impedance, the conductance and the capacitance are determined by a bridge method. Two sets of apparatus cover the entire frequency range, the first from 100 Hz to 20 kHz and the second from 30 kHz to 3 MHz. Each set consists of a generator (Wayne Kerr S121 and 022D at low and high frequencies), an analyzer (Wayne Kerr A321 at low frequencies and Airmec Type 853 at high frequencies) and a bridge (Wayne Kerr B221 and B601 at low and high frequencies). This apparatus measures the two components of the impedance of the cell as if for an equivalent circuit in parallel connection. The complex dielectric constant is: $\epsilon^* = \epsilon' - j\epsilon''$ with ϵ' and ϵ'' as dielectric constant and absorption. The admittance, the reciprocal of the impedance, for a dielectric is:

$$A = C_0\omega\epsilon'' + jC_0\omega\epsilon'$$

where ω is the angular frequency ($\omega = 2\pi\nu$), C_0 the capacity of the empty cell, expressed in Farad and computed from the dimensions of the cell. The real and the imaginary part of the complex dielectric constant are related to the conductance and capacitance as follows: $G = C_0\omega\epsilon''$ in Mho; $C = C_0\epsilon'$ in Farad. The loss angle of the dielectric is defined as $\tan\delta = G/C\omega = \epsilon''/\epsilon'$.

INVESTIGATION OF THE EFFECT OF FREQUENCY

Theory

We recall briefly O'Konski's theoretical approach of the behavior of heterogeneous dielectrics.

Model and definitions. The interfacial conduc-

tivity may be defined as a sum of two conductivities. The first as the conductivity due to the charge carriers in the immediate vicinity of the surface:

$$\lambda_1 = \sum_i s_i u_i z_i \tag{1}$$

where s_i is the number of carriers per unit surface of type i , u_i and z_i the mobility and the valence. The second conductivity is due to the existence of a double layer in the interface and is defined as an excess conductivity:

$$\lambda_a = \int_a^\infty (K' - K) dy \tag{2}$$

where K' is the conductivity at a given distance from the surface, and K is the conductivity of the equilibrium solution where the electrical potential resulting from the surface charge density is equal to zero. The lower limit of the integral sign is the distance, a , representing the thickness of the zone of conductivity λ_1 . The total effect of the surface charge density on the conduction is thus represented as the sum of λ_1 and λ_a .

Surface conductivity of systems with spherical particles. The dispersed phase consists of uniform spheres of radius, a , dielectric constant ϵ'_2 , conductivity K_2 and a surface conductivity λ_s ; the dispersing phase is characterized by ϵ_1 and K_1 .

It is supposed that the Laplace equations for the internal and external potentials are valid. The expressions of these potentials, using Böttcher's (1952) boundary conditions, lead to the equations describing the dielectric behavior of the system. In the expressions of the potentials, it is seen that the term $8\pi j\lambda_s/a\omega$ is always subtracted from ϵ_2^* . Thus the effect of the surface conductivity leads to an increase of K_2 , according to the following equation:

$$\epsilon_2^* - 8\pi j\lambda_s/a\omega = \epsilon_2' - j \left[\frac{4\pi}{a} \left(K_2 + \frac{2\lambda_s}{a} \right) \right] \tag{3}$$

These equations are similar to those derived by Wagner (1913, 1914), with the understanding that the sum of the conductivities is equivalent to the conductivity of the sphere in Wagner's treatment, (equivalent sphere).

Surface conductivity of systems with ellipsoidal particles. Fricke and Sillars's expression for randomly oriented isotropic ellipsoidal particles may be adapted to anisotropic particles having a surface charge density:

$$\epsilon^* - \epsilon_1^* = \frac{1}{3} p \sum \frac{\epsilon_i^* - \epsilon_1^*}{1 + A_i(\epsilon_i^* - \epsilon_1^*)/\epsilon_1^*} \tag{4}$$

where ϵ^* is the gross complex dielectric constant of the system; ϵ_1^* is the complex dielectric constant

of the liquid phase; ϵ_i^* is the complex dielectric constant of the equivalent ellipsoid in the axis i ; A_i is the depolarization factor in the axis i , and p the volume fraction. ϵ_i^* has the following explicit expression (according to O'Konski):

$$\epsilon_i^* = \epsilon_i' - j \left(\frac{4\pi K_i}{\omega} \right) \tag{5}$$

with: ϵ_i' is the dielectric constant of the equivalent ellipsoid, and K_i the effective conductivity of the charged particle equal to the sum of two conductivities: $K_i = K_i^o + K_i'$, where K_i^o is the conductivity of the ellipsoid which depends on the axis under consideration; K_i' is the surface conductivity and is related to the surface conductance of an oblate ellipsoid by the following expressions:

$$K_a' = \frac{2\lambda_s}{b} \quad \text{and} \quad K_b' = \frac{4\lambda_s}{\pi a} \tag{6}$$

The depolarization factors for the different axes are interrelated through the following expression:

$$A_a + A_b + A_c = 1. \tag{7}$$

When the imaginary parts are separated from the real parts of the initial equation, the two following expressions are obtained:

$$\frac{\epsilon''\epsilon_1' + \epsilon'\epsilon_1''}{(\epsilon_1'')^2 + (\epsilon_1')^2} = 1 + \frac{1}{3}p \sum_i \frac{(\epsilon_i'' - \epsilon_i')[\epsilon_1''(1 - A_i) + A_i\epsilon_1'] + (\epsilon_2' - \epsilon_2')[\epsilon_1'(1 - A_i) + A_i\epsilon_2']}{[\epsilon_1''(1 - A_i) + A_i\epsilon_1']^2 + [\epsilon_1'(1 - A_i) + A_i\epsilon_2']^2} \tag{8}$$

$$\frac{\epsilon'\epsilon_1'' - \epsilon''\epsilon_1'}{(\epsilon_1'')^2 + (\epsilon_1')^2} = \frac{1}{3}p \sum_i \frac{\epsilon_2'\epsilon_1'' - \epsilon_1'\epsilon_2'}{[\epsilon_1''(1 - A_i) + A_i\epsilon_1']^2 + [\epsilon_1'(1 - A_i) + A_i\epsilon_2']^2} \tag{9}$$

Three unknowns appear in these two equations: ϵ_2' the dielectric constant of the equivalent ellipsoid; ϵ_1'' the dielectric absorption of the equivalent ellipsoid proportional to K_i , the conductivity in the axis i ($i = a$ and b) and A_i the depolarization factor. If the left hand side of equation (9) equals zero, the case of a clay mineral system, one may solve these equations:

$$\epsilon_1'\epsilon_1'' - \epsilon''\epsilon_1' = 0$$

$$\epsilon_2'\epsilon_1'' - \epsilon_1'\epsilon_2' = 0$$

with the result $\epsilon_1'' = \frac{\epsilon_2'}{\epsilon_1'}\epsilon''$ (10)

when this result is put into equation (8) one obtains:

$$C = \frac{3}{p} \left[\frac{\epsilon''\epsilon_1'' + \epsilon_1'\epsilon'}{(\epsilon_1'')^2 + (\epsilon_1')^2} - 1 \right] = \sum_i \frac{\epsilon_2' - \epsilon_1'}{A_i\epsilon_2' + (1 - A_i)\epsilon_1'} \tag{11}$$

which is a function of ϵ_2' . The value of C is experimentally accessible. By giving different values to the depolarization factor, which are on the one hand physically plausible in the case of a clay mineral and on the other hand are allowed to differ as much as is reasonable, it is observed that the value of ϵ_2' varies only slightly.

Thus the value of A_a may be extrapolated to 1 and A_b tends to zero. This means that the depolarization effect exists essentially in the direction of the axis $2a$, perpendicular to the surface of the platelet. The electrical field action is effective in the direction tangential to the clay platelet. Introducing the simplification into the initial equation one obtains for the conductivity:

$$K_2 = K_1 + \frac{3}{2p}(K - K_1) \tag{12}$$

where K_2 is the specific conductivity in the direction of the axis $2b$ and equal to

$$K_2 = K_2^o + \frac{4\lambda_s}{\pi a} \tag{13}$$

with K_2^o the specific conductivity of the particle in $2b$. In highly hydrated systems, such as clay gels, it seems to be acceptable to think that this term is negligible against K_2 . Thus K_2 corresponds to the specific surface conductivity:

$$K_2 = K_s = \frac{4\lambda_s}{\pi a} \tag{14}$$

with λ_s as surface conductance.

In order to solve equation (12), K_1 the specific conductivity of the dispersing phase has to be known. This phase will be defined as the supernatant obtained by centrifugation; the resulting conductivities are: lithium clay 98.0 Mh ocm^{-1} ; sodium clay 143.6 Mh ocm^{-1} ; potassium clay 188 Mh ocm^{-1} ; and cesium clay 127.8 Mh ocm^{-1} .

Results

The variation of the specific conductivity of the clay gel, K_g , as a function of the frequency is rather small, Fig. 1. On the contrary, the absorption ϵ'' varies very largely and is characteristic of a conduction of free charge carriers (Freymann and Soutif, 1960).

No dielectric absorption, maximum in the plot ϵ'' vs. $\log \nu$ has been detected in the used frequency

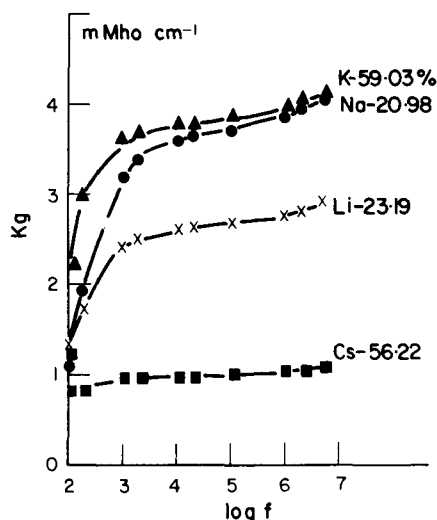


Fig. 1. Specific conductivity of 4 clay gels as a function of frequency at 25°C.

range. According to the theoretical approaches, a different maximum per each axis should be present. In the case of a clay mineral, one might expect two absorptions, or at least one for the longest axis. The fact that none is observed renders any interpretation of the data at least difficult if not impossible in the framework of the present theory. The high value of the conductivities of the system may possibly obscure these maxima.

The variation of K_g and K_s , as functions of the clay concentration are represented in Fig. 2 and Fig. 3. K_g vs. clay concentration shows a sigmoidal curve (Cremers, 1964), while K_s has a maximum. The behavior of the lithium clay is rather unexpected, no explanation has been found for it. The maximum of K_s corresponds to the region where K_g is increasing the most rapidly. It seems that, at a certain gel concentration, the current transport is more efficient as a result of an optimum contact of the conduction zones, Table 1.

Through the use of equation (14), the surface conductance λ_s may be calculated if the value of the semi-axis a , is known. The choice of this value is rather difficult in the case of the swelling lithium and sodium clays. It is impossible to evaluate the interlamellar distance by X-ray diffractometry. However, when the tangential character of the conduction is taken into consideration, the conduction will be limited to a rather thin zone. If 4 monolayers of water are assumed, then $2a = 30 \text{ \AA}$, the value of λ_s is of an order of 10^{-9} Mho. In the case of potassium and cesium clay, the interlamellar distances have been measured and are respectively 17 \AA and 15 \AA . If 2 monolayers are taken, then $2a = 20 \text{ \AA}$, the value of λ_s is also of an order of

Table 1. Specific conductivity of the gel K_g , specific surface conductivity K_s , and surface conductivity λ_s , as a function of the clay concentration at 1000 Hz

	Concs. (%)	K_g , mMho cm ⁻¹	K_s , mMho cm ⁻¹	λ_s , Mho	
Li	9.18	0.85	30.30	$3.57 \cdot 10^{-9}$	
	11.10	1.20	36.20	4.26	
	16.50	2.06	41.70	4.91	
	19.08	2.26	39.05	4.60	
	23.19	2.44	33.80	3.98	
	31.82	2.88	27.50	3.24	
	41.79	3.16	21.40	1.52	
	52.24	2.98	16.65	1.96	
Na	12.02	1.45	39.40	$4.64 \cdot 10^{-9}$	
	20.98	3.22	50.00	5.89	
	31.23	9.91	38.20	4.50	
	32.54	4.18	38.80	4.57	
	37.64	4.35	33.60	3.96	
	49.85	4.38	23.20	2.73	
	K	23.72	1.82	23.20	$1.82 \cdot 10^{-9}$
		26.30	2.32	27.60	2.17
29.92		2.82	28.20	2.21	
34.92		3.24	26.85	2.11	
36.25		3.25	25.80	2.02	
38.89		3.39	24.50	1.92	
46.08		2.82	18.40	1.43	
59.03		3.60	14.50	1.14	
Cs	22.85	0.50	5.77	$0.45 \cdot 10^{-9}$	
	30.46	0.71	6.24	0.49	
	32.90	0.72	5.84	0.46	
	41.67	0.72	4.27	0.34	
	41.73	0.81	4.85	0.38	
	47.68	0.67	3.31	0.26	
	56.22	0.93	3.78	0.30	

10^{-9} Mho; a value generally accepted for the surface conductance.

Up to now, only salt free systems have been studied; however, it may be interesting to have a closer look at systems with a definite double layer. The presence of electrolyte in the interfacial region extends considerably the conduction zone, therefore, a true volume conduction is possible. Thus it becomes difficult to define a surface conductivity and in order to keep the model of the equivalent ellipsoid, it is necessary that the extension of the double layer be relatively small in comparison with the size of the clay particles. Then the volume conduction will occur in a thin region and may be assimilated to a surface conductivity.

The application of the theory seems thus to be more rigorous in the case of salt free systems. In these ones, the initial assumptions of the theory are certainly more nearly correct.

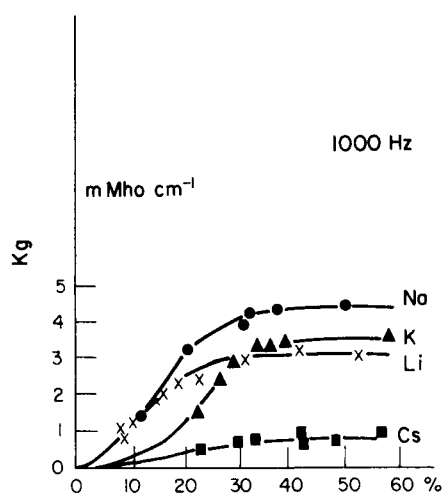


Fig. 2. Specific conductivity as a function of clay concentration for the 4 clay systems, at frequency 1000 Hz and 25°C.

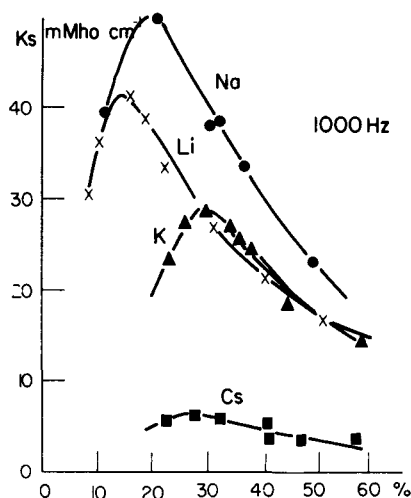


Fig. 3. Specific surface conductivity as a function of clay concentration for the 4 clay systems, at 1000 Hz and 25°C.

INVESTIGATION OF THE EFFECT OF TEMPERATURE

Experimental results

Plots of $\log \epsilon''$ vs. $1/T$. As an example, such plots are shown in Fig. 4 for sodium montmorillonite at a series of clay concentrations. The variation of the $\log \epsilon''$ vs. the reciprocal of the absolute temperature is linear, and enables the calculation of the Arrhenius activation energy. The results are summarized in Table 2.

Table 2. Activation energies (E_A) in kcal/mol. of the high temperature region (H.T.), intermediate temperature region (I.T.) and low temperature region (L.T.) at 1000 Hz

	(%)	$E_{A,H.T.}$	$E_{A,I.T.}$	$E_{A,L.T.}$
Li	9.18	4.56	7.34	6.11
	20.60	4.08	11.95	6.49
	22.04	3.92	12.61	6.29
	31.84	3.43	13.38	6.28
	39.98	3.98	14.30	6.33
	44.32	4.00	14.38	6.90
	53.58	4.16	14.38	6.23
Na	13.59	4.21		
	14.76	4.56		
	24.10	3.68	12.90	5.64
	29.30	3.81	13.25	5.84
	40.50	3.74	13.77	5.31
	49.58	4.01	14.70	5.07
	53.92	4.15	14.65	5.05
	60.90	4.38	15.10	4.97
K	18.30	4.68		
	22.46	4.56	7.66	5.43
	23.42	4.47	6.38	4.66
	29.51	4.47	8.56	4.59
	38.90	4.10	11.58	4.94
	43.33	4.20	12.20	5.45
	55.18	4.16	12.56	4.81
	59.16	4.43	13.41	5.30
Cs	22.74	4.06	5.02	5.02
	28.57	3.74	5.70	5.70
	33.80	3.88	6.93	5.69
	44.42	4.20	10.40	6.29
	45.36	4.38	10.20	6.34
	49.42	4.47	11.67	6.38
	61.39	4.75	12.59	6.28

Three distinct regions are observed. The first from 145°K up to 200°K which will be called the region of low temperature; the second from 200°K up to 273°K, the intermediate temperature region, and the third above 273°K, the high temperature region. The first two regions concern the temperature range in which the gel may be considered as a solid in a sense which will become apparent. The slopes in these regions have different values and it should be stressed that the high value of the slope, and thus the high activation energy, appear in the intermediate temperature region where the thermal energy is higher. The transition temperature between the two regions is $200 \pm 4^\circ\text{K}$ in the explored clay concentration range. A minimum clay concentration is reached below which these transitions disappear. This minimum varies with the nature of the sorbed ion. With changing fre-

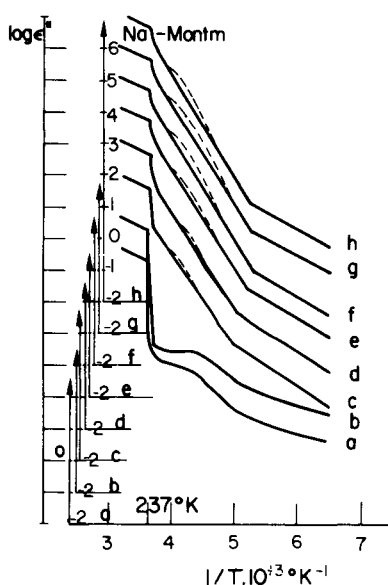


Fig. 4. Plots of $\log \epsilon''$ vs. $1/T$ for a sodium montmorillonite system at 1000 Hz. Clay concentrations are: a—13.59, b—14.76, c—24.10, d—29.30, e—40.50, f—49.58, g—53.92, h—60.09.

quency (100 Hz–20 kHz), the slope and the general appearance of the graphs do not vary. In the vicinity of 273°K, the conductivity increases very sharply over an interval of 6°K. The height of this jump decreases with increasing clay concentration and at constant clay concentration, the value increases in the following order:

$$\text{Cs} > \text{K} > \text{Na} > \text{Li}.$$

Plots of $\tan \delta$ vs. T . An example of such plots is shown in Fig. 5 for lithium montmorillonite at different clay concentrations. Several absorption peaks appear in the temperature range below 273°K. Two distinct peaks exist. The first, in the low temperature range, is a broad peak, with a rather small value for $\tan \delta$ (between 1 and 2); it is impossible to calculate the activation energy of these absorptions for they are too flat to locate with any accuracy the corresponding temperature. The second peak, in the intermediate temperature range, close to 273°K, may reach values of $\tan \delta$ up to 60 and 70, especially for lithium and sodium systems. In the lithium and cesium clays, the main peak is a composite peak, a small one appears at a lower temperature; for sodium and potassium, the latter is absent. With increasing frequency, the peaks shift to higher temperatures; so, the one in the low temperature region will disappear at a frequency of 2000 Hz, for it would be located in the intermediate temperature region where,

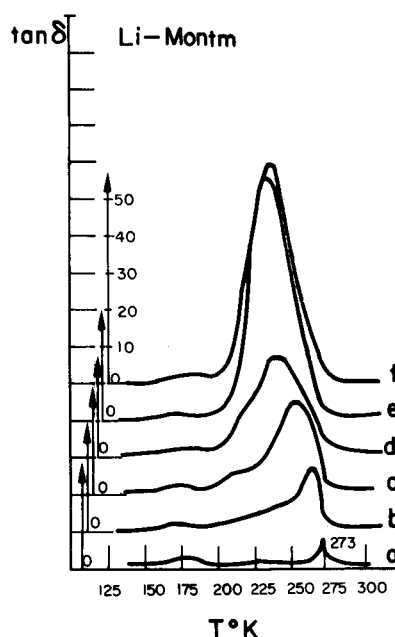


Fig. 5. Plots of $\tan \delta$ vs. T for a lithium montmorillonite system at 100 Hz. Clay concentrations are: a—19.18; b—20.60; c—22.04; d—31.84; e—39.98; f—44.32.

obviously, other phenomena occur. The maxima in the intermediate temperature region, however, will with increasing frequency, never extend beyond 273°K.

Plots of $\log \epsilon'$ vs. $1/T$. Below 273°K, no linearity has been observed; up to 180°K, the value of $\log \epsilon'$ is almost constant. Above 180°K, the curve shows apparently sigmoidal parts, as shown in the example for potassium montmorillonite, in Fig. 6. The temperature of the inflection corresponds to the temperature of the maximum of $\tan \delta$, and this is generally true in the low temperature range. However, the large absorption of $\tan \delta$ in the intermediate temperature region does not, necessarily, correspond to particular variation in the curve $\log \epsilon'$, and renders any interpretation more difficult.

Discussion

In the presentation of the results below 273°K, it has been stressed that the slopes of small value are situated in the low temperature region and the slopes of high value in the intermediate temperature region. Thus, the activation energy required for the process is the lowest in the low temperature region.

When the conductivity or the diffusion coefficient over a wide temperature range is measured in ionic crystals containing a number of impurities, a similar variation of the activation energy is

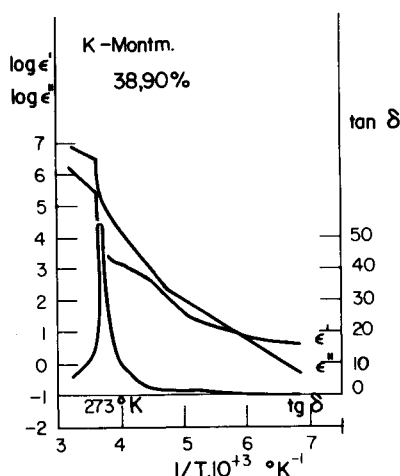


Fig. 6. Comparative plots of $\log \epsilon'$, $\log \epsilon''$ and $\tan \delta$ vs. $1/T$ for a potassium montmorillonite gel, at 1000 Hz.

observed. In this case, the low temperature region is called the *extrinsic region* and the intermediate temperature region, the *intrinsic region* (Shewmon, 1963; Girifalco, 1964). The experimental activation energy in the intrinsic region is the sum of two activation energies (E_A).

$$E_A - \text{experimental} = \frac{1}{2}E_A - \text{creation} + E_A - \text{displacement}$$

where the activation energies of creation and displacement concern the migrating lattice defect.

In the study of the surface conductivity, it has been shown that the cationic motion occurs in a thin water layer. If one supposes that the presence of the sorbed ion has a perturbing effect on the water structure, then this leads us to consider the cation as an impurity. It is the principal cause of the lattice defects in the water structure, which imply conduction by protons in this temperature range. This hypothesis enables us to interpret the succession of the activation energy in a consistent way, say, the nature of the conduction is the same over the considered temperature range.

It is during the phase change at 273°K, where the jump of the conduction occurs, that progressively the adsorbed cation participates in the conduction. Once 273°K is reached, the conduction is predominantly cationic.

The nature of these two types of conduction can account for reversing the order of the activation energies below and above 273°K, as a function of the counterion.

$$E_A - \text{Li clay} > E_A - \text{Na clay} > E_A - \text{K clay} > E_A - \text{Cs clay}$$

The above order is found in the intrinsic region and is reversed at temperatures above 273°K.

This interpretation, ultimately hypothetical in its present form, accounts for the different experimental results. It is, however, too early to decide which type of lattice defect (rotational or translational) is responsible for the conduction, (Freyman and Soutif, Gränicher *et al.*) or what role is being played by the sorbed cation in ordering its surrounding water molecules.

Concerning the plots of $\tan \delta$ vs. T and of $\log \epsilon'$ vs. $1/T$, it seems difficult to give a rigorous interpretation. The absorption of $\tan \delta$ in the low temperature region may be interpreted as a Debye dipolar absorption and is then to be attributed to the water molecules, (Freyman and Soutif; Gränicher *et al.*; Debye, 1929; Fröhlich, 1958). As to the large absorptions in the intermediate temperature region, it is, however, impossible to decide on their physical origin. It does seem that a relation exists between the values of $\tan \delta$ and the swelling character of the system.

It will be of great interest to investigate this complex problem more deeply.

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Résumé— La conductivité en surface de colloïdes d'argile montmorillonite sans sel, saturés au lithium, sodium, potassium et au césium a été étudiée. La théorie du comportement de diélectriques hétérogènes adaptés aux systèmes ayant une densité de charge en surface, a été appliquée aux colloïdes d'argile. D'après les calculs numériques, il était évident que la valeur du facteur de dépolarisation pouvait être extrapolée à une, dans le sens du petit axe de la plaquette, ce qui signifie que dans cette direction le champ d'action devient zéro. Toutefois, le long de l'axe le plus long, l'action est complète et le mouvement des porteurs de charge est surtout tangentiel à la plaquette. Les valeurs de la conductance de surface sont de l'ordre de 10^{-9} Mho.

La recherche du comportement des molécules d'eau a été faite pour une gamme étendue de températures (145–320°K). A des températures inférieures à 273°K, la conduction paraît être surtout protonique; les contre-ions sont considérés comme éléments perturbateurs dans les structures des couches d'eau créant ainsi un réseau de défauts capables d'entraîner le courant. Au-dessus de 273°K, la conduction est essentiellement due aux cations absorbés, leur contribution commençant au moment du changement de phase.

Kurzreferat— Die Oberflächenleitfähigkeit von salzfreien, mit Lithium, Natrium, Kalium und Cäsium gesättigten Montmorillonit-Ton-Gelen wurde untersucht. Die Theorie des Verhaltens heterogener Dielektrika, angepasst an Systeme mit Oberflächenladungsdichte, wurde auf die Ton-Gele angewendet. Aus zahlenmässigen Berechnungen ergab sich, dass der Wert des Depolarisierungsfaktors in der Richtung der kurzen Achse des Plättchens bis zum Wert eins extrapoliert werden kann, wodurch ausgesagt wird, dass die Feldwirkung in dieser Richtung null ist. Entlang der langen Achse ist die Wirkung jedoch vollständig und die Bewegung der Ladungsträger ist im wesentlichen tangentiell zum Plättchen. Die Werte der Oberflächenleitfähigkeit sind in der Grössenordnung von 10^{-9} Mho.

Die Untersuchung des Verhaltens von Wassermolekülen wurde innerhalb eines weiten Temperaturbereiches von 145–320°K durchgeführt. Bei Temperaturen unterhalb 273°K scheint die Leitung vorwiegend protonisch zu sein; die Gegenionen werden als Störellemente in den Wasserschichtgefügen betrachtet, die eine Anzahl von Gitterdefekten schaffen, durch welche Leitung des Stromes ermöglicht wird. Oberhalb 273°K wird die Leitung im wesentlichen durch die adsorbierten Kationen besorgt, deren Beitrag während des Phasenwechsels beginnt.

Резюме—Исследовалась поверхностная проводимость не содержащих соли монтмориллоновых глинистых гелей, насыщенных литием, натрием, калием и цезием. Теория поведения гетерогенных диэлектриков, приспособленная для систем, обладающих поверхностной плотностью заряда применялась в случае глинистых гелей. Числовое вычисление ясно показало, что значение коэффициента деполяризации может быть экстраполировано до единицы по направлению малой оси пластиночки, а это означает, что действие поля в этом направлении равняется нулю. Однако, вдоль длинной оси действие полное и движение носителей заряда в сущности тангенциально к этой пластинке. Значения поверхностной проводимости порядка 10^{-9} мксим.

Исследование поведения молекул воды проводилось в широком температурном диапазоне (145–320°K). При температурах ниже 237°K, проводимость как видно преимущественно протонная; противоионы считают расстраивающими элементами в структурах водяного слоя, образуя тем самым ряд дефектов решетки, которые могут переносить ток. Свыше 273°K, проводимость является по существу следствием адсорбированных катионов, причем содействие их начинается во время фазового превращения.