# Dielectric Behavior of Kaolinite and Dickite

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Examination of the measured values discloses that the splittings for the ethyl derivatives may be fitted within experimental error by the equation

$$J_{CH_3-CH_2} = 8.4 - 0.4E,$$

where $E$ is the Huggins electronegativity[5] of the atom directly attached to the ethyl. Similarly for isopropyl derivatives

$$J_{CH_3-CH} = 8.0 - 0.55E.$$

From these observations and others[6] a crude but useful generalization may be made; i.e., the spin-spin interaction in a molecule is changed only very slightly by the alteration of nonmagnetically active substituents, while introduction of a new magnetically active nucleus may completely change the nuclear interaction functions.

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[3] Bene, Denis, and Extermann, Physica 17, 308 (1951).
[4] B. A. Jacobsohn and R. K. Wangsness, Phys. Rev. 73, 942 (1948).
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[6] Unpublished data of the authors. Also see McConnell, Reilly, and McLean, J. Chem. Phys. 24, 479 (1956); Schoolery, Discussions Faraday Soc. 19, 215 (1955).

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## Dielectric Behavior of Kaolinite and Dickite

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A GOOD number of properties of crystals are directly related to lattice defects such as vacancies, interstitials, dislocations, etc. As was pointed out by Dekeyser,[1] defects in clay minerals have never been considered in attempts to correlate their properties with their structure. The obvious reason for this state of affairs is that practically nothing is known about defects in such compli-cated lattices, mainly because most of the methods for studying defects in simpler types of crystal cannot be applied to clays. As relaxation effects in the dielectric properties of ionic crystals can yield information about some of the defects they contain, and as the method can be used with powders, we applied this method to clay minerals. In this note we report results obtained for kaolinite and dickite. The minerals, of which the fractions $<2\mu$ were used, originated, respectively, from Cornwall and San Juanita, Mexico. They were brought in suspension in water and other organic liquids (benzene, benzene-alcohol). From this suspension a thin layer was evaporated on a 1-mm copper plate and kept for several days at 70°C in a vacuum. The specimen is then transferred to a vacuum cell which can be heated up to 300°C. The copper plate on which it is deposited is one of the electrodes of the condenser on which the $tg\delta$ is measured as a function of frequency and temperature; the other electrode is strongly pressed against the free surface of the sample. All measurements are performed in vacuum. The bridge used covers a frequency range of 100 cps to 200 kc/sec.

With this arrangement we examined a good number of samples from the same kaolinite. The general form of the results is shown in Fig. 1 (a, b, and c). We see that the dissipation factor for a given temperature passes through a maximum, which shifts to higher frequencies at which we cannot measure with the present apparatus. The extension of the frequency range, which is already undertaken, will show the behavior of the $tg\delta$ versus frequency curves at higher frequencies. The frequency maxima at 62°, 82°, 102°, 116°, and 150°C are, respectively, at 750 cps, 3 kc/sec, 12 kc/sec, 10 kc/sec, and 70 kc/sec. The relationship between the maximum frequency $\nu_{max}$ and the reciprocal temperature $(1/T)$ has a simple form. It can be represented by[2]

$$2\pi\nu_{max}\tau_0 = e^{-U/kT}.$$

From this relation we can deduce the activation energy $U$ which is for the studied sample of kaolinite $K50$, 0.65 ev.

Also we examined several samples from dickite. This clay mineral has an analogous structure as kaolinite, but the behavior
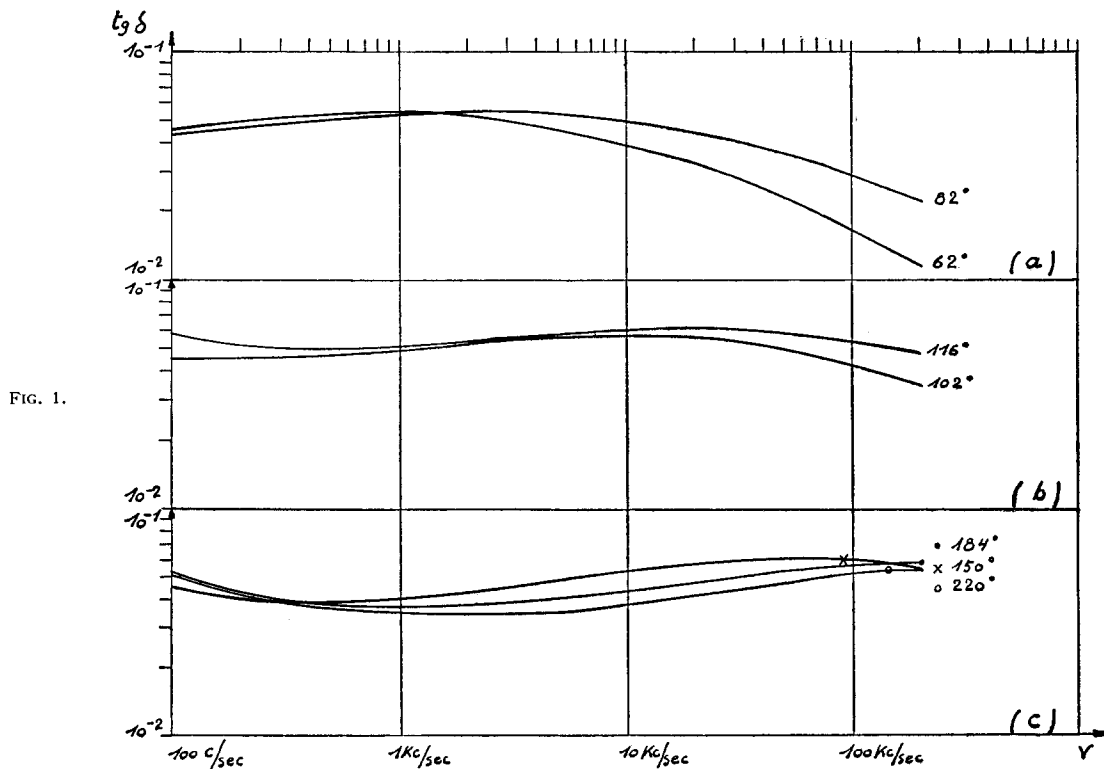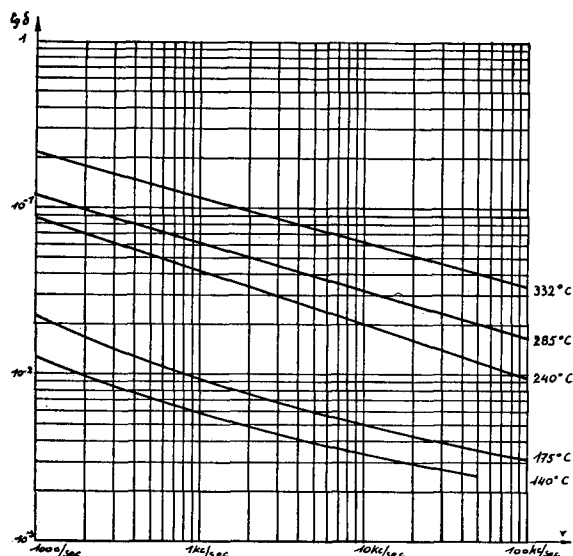


FIG. 1.

FIG. 2.

of its dielectric properties is quite different. The curves $tg\delta$ *versus* frequency at different temperature give no maximum as shown in Fig. 2.

Further investigations are in progress and will be published in a later paper. Measurements are in progress on kaolinites and dickites of different origin in order to see to what factor the observed effects are due.

We wish to thank Professor Dr. W. Dekeyser, who suggested this study, for his interest and encouragement. We also thank I.R.S.I.A. (Brussels) who sponsors the Comité pour l'éstablissement de la carte des sols et de la végétation de la Belgique.

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# On the Double-Maxima Distribution of Deutero-Paraffins
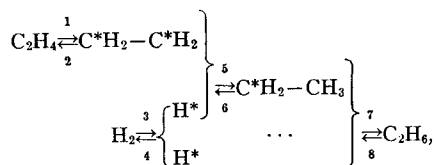
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THE distribution of deutero-paraffins in the catalytic deuteration of olefins was found first by Turkevich et al.,[1] and its mechanism has been discussed by many authors.[1-3] A new type of distribution with double maxima has further been observed by Bond and Turkevich,[4] who studied the reaction of a mixture having the composition $C_3H_6$, 51.5%; $C_3D_6$, 41.5%, and $C_3HD_5$, 7.0%.

The writer would like to give here an explanation of this particular distribution on the basis of the mechanism[4] formerly proposed by himself to explain the earlier experimental results.

For the sake of simplicity, it will be illustrated for the case of ethylene. The reaction between hydrogen and ethylene takes place with the scheme,

$$C_2H_4 \overset{1}{\underset{2}{\rightleftharpoons}} C^*H_2-C^*H_2 \left\{ \begin{matrix} \overset{5}{\underset{6}{\rightleftharpoons}}C^*H_2-CH_3 \\ \cdots \end{matrix} \right. \overset{7}{\underset{8}{\rightleftharpoons}} C_2H_6,$$

$$H_2 \overset{3}{\underset{4}{\rightleftharpoons}} \left\{ \begin{matrix} H^* \\ H^* \end{matrix} \right.$$

where an asterisk denotes a chemisorbed bond. Assuming that the isotopic replacement does not alter the rates of respective

reactions $V_i$, the steady-state conditions relating to each intermediate may be stated as follows.

$$(2V_4+V_6+V_7)y(D^*) = V_3[2y(D_2)+y(HD)]$$
$$+V_6[y(C_2D_5^*)+\cdots+\tfrac{1}{3}y(C_2H_4D^*)]$$
$$+V_8[y(C_2D_6)+\cdots+\tfrac{1}{6}y(C_2H_5D)]$$

$$(V_2+V_5)y(C_2H_4^{**}) = V_1y(C_2H_4)+V_6[y(C_2H_5^*)+\tfrac{1}{3}y(C_2H_5D^*)]$$

$$(V_6+V_7)y(C_2H_5^*)$$
$$= V_5y(H^*)y(C_2H_4^{**})+V_8[y(C_2H_6)+\tfrac{1}{3}y(C_2H_5D)],$$

where $y$ denotes the fraction of each isomer. Putting $y(D_2)=1$, $y(C_2H_4)=y(C_2D_4)=\tfrac{1}{2}$ in the foregoing equations, and eliminating $y$'s of the intermediates, we have immediately the ratio of the rates of hydrogen formation at the stage of the reaction as follows.

$$H_2:HD = V_4y(H^*)^2 : 2V_4y(H^*)y(D^*) = 1:2\Omega,$$
$$\Omega \equiv y(D^*)/y(H^*).$$

Assuming further that $V_1 \cong V_2 \gg V_i (i=3,4,\cdots,8)$ and $V_3 \ll V_7 \ll V_6 \cong V_5$, we have similar expressions for ethanes and ethylenes approximately,

ethanes; $d_0:d_1:d_2:d_3:d_4:d_5:d_6 \cong 1:2\Omega:\Omega^2:2R\Omega^2:1+R\Omega^2:2\Omega:\Omega^2$

ethylenes; $d_1:d_2:d_3 \cong 1:R:1$

$$\Omega \cong (6V_3+V_6)/V_6 = 1+6V_3/V_6 > 1 > R = y(D^*)V_6/3V_2, R\Omega < 1.$$

From these relations it follows that the distribution of paraffins has always two maxima at $d_2$ and $d_{N+2}$ if $\Omega \gg 1 (V_3 \gg V_6)$, or at $d_1$ and $d_{N+1}$ if $\Omega$ is greater than but near to unity $(V_3 \ll V_6)$, that hydrogen deuteride predominates over hydrogen, and that the distribution of deutero-olefins has a minimum at $d_{N/2}$. These conclusions may be applicable to the cases of ethylene $(N=4)$, propylene $(N=6)$, and cis-2-butene $(N=8)$.

It should be noted that the random distribution[2] could not explain this particular distribution, because it yields always one maximum.

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# Differential Capacitance in Electrolytes

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IN connection with differential capacitance $(C^{(d)})$ measurements in a methanol solvent, Grahame[1] recently postulated that the rapid increase observed in $C^{(d)}$ with sufficiently negative potentials, arises from electrostriction which separates charge centroids of the solvent molecule and hence increases the effective dielectric constant of the inner region next to the cathode.

Another explanation,[2] which shows good agreement with experiment for water solvent, is based on the different assumption that the internal field causes solute ions to press against the inner layer and decrease its thickness, with a consequent increase of $C^{(d)}$. This compression is not of major importance until sufficiently negative potentials are reached that dielectric saturation of the solvent molecules in the inner layer is substantially complete. The interplay of diffuse-layer capacitance, dielectric saturation, and inner-layer compression also accounted well for the characteristic maximum of $C^{(d)}$ observed at low solute concentrations in water.[2,3]

Since Grahame's type of electrostriction depends upon the dipole moment of the solvent molecule, which interacts much less strongly with the internal field than do charged ions adjacent