HYDROGEN-DEUTERIUM EXCHANGE IN CLAYS AND PROBLEMS IN THE ASSIGNMENT OF INFRARED FREQUENCIES IN THE HYDROXYL REGION[1]

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EXTENDED ABSTRACT

In spite of the considerable interest and work with infrared absorption spectra not much reliable correlation has as yet been made between these spectra and other properties of the clays. Where generalizations have been made they have been based on a few samples and not the best-quality patterns. An examination of the "hydroxyl region" of the infrared spectra of montmorillonites in various states of dehydration, kaolin family minerals, brucite, gibbsite and other hydroxides and clays was made on the Perkin-Elmer model 21 double-beam spectrometer, employing samples mixed with KBr and pressed into discs.

Resolution of several maxima in the hydroxyl region of powder spectra of brucite (2.33, 2.47, 2.68, 2.8, 3.03, 3.4?, and 3.96 microns) was obtained. $Mg(OD)_2$ synthesized under high temperature and D_2O pressure revealed a similar spectrum, with maxima present at higher wave lengths which are multiples (1.37 times) of the corresponding $Mg(OH)_2$ wave length (3.18, 3.35, 3.65, 3.84, 4.08, and 4.2 microns) with a trace of the 2.68 micron $(OH)^-$ absorption maximum. Resolution of three strong maxima at 2.673, 2.708, and 2.732 microns was obtained for dickite, and in addition weaker maxima at 2.2 and 2.9 microns. Kaolinite spectra obtained were similar, with the principal maxima at 2.678, 2.700, and 2.727 microns not as well resolved. Differences between the intensity patterns of the maxima for the two minerals are characteristic.

That there is no simple correlation between the complex absorption spectrum of brucite and the established x-ray structure has already been pointed out by Mara and Sutherland (1953). Reconfirmation of the brucite structure including a difference Patterson synthesis to locate hydrogens has recently been completed by H. E. Petch and H. D. Megaw (personal communication), and shows that the discrepancy cannot be explained by assuming an incorrect x-ray structure. In recent papers (Auskern and Grimshaw, 1955; Wadsworth, Mackay, and Cutler, 1955, Dietzel [see Hofmann, this volume]) various authors have proposed the assignment of the different absorption frequencies in the (OH) region to structurally different hydroxyls. For example, the two (sic) maxima in the kaolinite spectrum are assumed to be related to "inner" and "outer" hydroxyls. On the basis of the brucite example such conclusions are already suspect. Further, the fact that higher resolution spectra reveal definitely more than two absorption bands also

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speaks against these hypotheses. Still more evidence is adduced from the exchange experiments described below.

H-D exchange in layer silicates was studied in several minerals as a function of time, temperature, and pressure (in simple hydrothermal apparatus described by Roy and Osborn, 1952). Kaolinite and dickite treated with D_2O at room temperature showed less than $\frac{1}{2}$ percent replacement of $(OH)^-$ by $(OD)^-$ in as long as five days, while about 2 percent of the $(OH)^-$ in montmorillonite was exchanged. Considerable exchange, however, takes place in the 3 minerals at elevated temperatures in as short a period as one day: In kaolinite treated for three days at 370° C at approximately 20,000 psi D_2O replacement is greater than 50 percent, in montmorillonite less than 50 percent, and in dickite the least.

A comparison of the OH and OD absorption frequencies in a series of partly exchanged samples shows that:

1. The exchange at room temperature into well-ordered hydroxyl positions is very limited, whereas at elevated temperatures it is rapid and extensive.

2. The absorption frequencies are related by the usual factor of 1.37.

3. The relative intensities of the three main maxima are the same in the OD region as in the original OH region.

4. With progressively greater exchange the ratios of the absorption maxima (in the OH region) do not change; in fact, the increasing absorption maxima in the OD region bear the same relative ratio to one another as do the OH maxima in the original OH material. This provides further evidence that the major absorption frequencies cannot be correlated with "inner" and "outer" hydroxyls since the "outer" OH frequency should diminish and the "outer" OD frequency should increase more rapidly than the "inner" counterparts.

Both exchange and dehydration experiments on montmorillonites show that the suggestions of Buswell and Dudenbostel (1941) and others regarding the assignment of the 2.7 micron absorption to "hydroxyl" and 2.9 micron absorption to interlayer water cannot be wholly correct. The patterns do show two main absorption maxima at 2.73 and 2.9 microns and the latter maximum decreases somewhat on dehydration, but even upon the loss of all interlayer water (checked by a simultaneous weight loss of 14 percent) the absorption is nearly as large as the 2.72 micron one. In partially (OD)-exchanged montmorillonites also the 2.9 micron absorption remains as strong (relative to the 2.72 micron) as in the original and it is certainly to be expected (as shown since by Faucher and Thomas, 1955) that the interlayer water will exchange with the D_2O). It may safely be asserted that the 2.9 micron absorption band is attributable to more than interlayer water and that the lattice OH is responsible to a considerable if not a major extent for this absorption also.

Other observations which can be made on the basis of these data are:

1. A correlation between hydrogen bond length (or "strength") and the wave length of the absorption maximum in the "OH region" is quite dangerous and where such a relationship holds it may be fortuitous. Thus the results of Rundle and Parasol (1952) and others may be valid for organic liquids but their application to solid hydroxylic minerals is fraught with difficulty, especially where there is a multiplicity in the spectrum.

2. If we can consider the effective exchange as that of $(OD)^-$ for $(OH)^-$

(which is a moot point) then the amount of exchange obtained herein should certainly set a maximum for the anion exchange possible in clays, for it is unlikely that any ion can be more similar to $(OH)^-$ than $(OD)^-$. This would suggest that the relatively high values obtained for F^- and $(PO_4)^{3-}$ exchange in clays should not properly be attributed to actual replacement within the lattice. The data obtained correlated reasonably with those of McAuliffe and others (1947). If their claim that surface (OH) ions exchange rapidly even at room temperature is correct, then since there is no equivalent infrared absorption, either the surface hydroxyls must show very unusual hydrogen bonding or the absorption may be spread over a wide frequency band.

3. At fairly high temperatures (200° to 300° C) the exchange of $(OD)^-$ for $(OH)^-$ is so rapid that it would suggest that methods involving the study of the H-isotope content of hot-spring and other possibly "juvenile" waters, must take into account the fact that if the water came into contact with any large amount of OH-containing minerals virtually complete exchange should be expected in a short time, so that the isotopic concentration of the hydrogen will reflect merely that of the dominant hydroxylic minerals.

ACKNOWLEDGMENT

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