

MINERALOGICAL NOTES

MICROPOROSITY OF MUSCOVITE SHEETS

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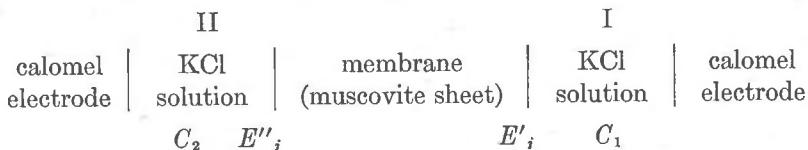
ABSTRACT

Micropores in mica sheets were evaluated by measurement of the membrane concentration potential. The pore radii is roughly characterized by the magnitude of Debye-Hückel length. By using thin mica sheets as a membrane it was established that they possess micropores of a diameter corresponding to the thickness of ionic atmosphere in 10^{-4} — 10^{-8} M/l uni-univalent solutions, i.e. a few hundred micrometers. They have a length of hundreds of micrometers.

Muscovite is a phyllosilicate, whose unit cell consists of silica (tetrahedra)-alumina (octahedra)-silica (tetrahedra) layers with a thickness along crystallographic *c* axis of 20 Å. In nature it is found in sheets up to several centimeters in thickness, which, due to perfect cleavage, can be split into thin sheets several microns in thickness.

It is known that all crystals have some defects: flaws, voids, vacancies, etc., which are not always possible to distinguish. These defects may be evident as fine (micro) pores whose size can be evaluated by physical and chemical methods.

The order of pore size in sheets like that of mica can be approximately determined by the membrane concentration potential (*E*), which is measured as the potential difference between two liquid junction potentials (*E'*_{*i*} and *E''*_{*i*}), using two calomel electrodes:



If $E'_i > E''_i$, and $C_2 > C_1$, then the pores are charged negatively, and vice versa. The membrane concentration potential (*E*), being the sum of the two junction potentials, *E'*_{*i*} and *E''*_{*i*}, is given by:

$$E = E'_i + E''_i = (2t_k - 1) \frac{RT}{F} \ln \frac{a'_{\pm\text{KCl}}}{a''_{\pm\text{KCl}}}$$

where:

t_k = transference number of K in the membrane; $a'_{\pm\text{KCl}}$ and $a''_{\pm\text{KCl}}$ activities of KCl on both sides of the membrane; R = gas constant; T = absolute temperature and F = Faraday constant.

The relation between E and the radii of the pores is complicated, nevertheless it can be accepted that the diffusion through pores of an electrolyte whose cation and anion mobilities are equal (*e.g.*, KCl), generates a membrane concentration potential, if the radius of the pores is of the same order as the thickness of the electrical double layer. The thickness of the electrical double layer is roughly characterized by the magnitude of the Debye-Hückel parameter $1/K$, where K is the Debye-Hückel reciprocal length. The values $1/K$ for KCl solutions of 10^{-1} , 10^{-2} , 10^{-3} , and 10^{-4} M are: 10, 30, 96, and 305 Å, respectively.

The membrane concentration potential depends on pore size and is independent of pore volume, therefore the potential may appear even if only one pore is present in the crystal. The conviction that mica crystals may have defects and that they are possible to detect only by using a thin sheet induced us to undertake the study of membrane concentration potential by using a thin muscovite sheet as membrane. The membrane concentration potential was measured with Keithley differential voltmeter 662, which permits infinite impedance at null for potentiometric measurements from 0 to 500 V; therefore the membrane resistance is not of importance in such measurements. The principal results are present in Table 1.

TABLE 1. MEMBRANE CONCENTRATION POTENTIAL

Origin	Thickness μm		E at $a''_{\pm\text{KCl}}/a'_{\pm\text{KCl}}$	
	Original	Cleaved	0.000190	0.00174
			0.000096	0.00090
Tucumán, semiclear ^a	430	—	17.1	13.4
Tucumán, semiclear	—	90	17.1	13.8
Tucumán, semistained ^a	580	—	0	0
Tucumán, semistained	—	152	10.8	7.3
Córdoba, stained ^a	505	—	0	0
Córdoba, stained	—	205	13.7	4.5
San Juan, stained ^a	209	—	14.5	6.0
Unknown ^b	—	20	12.9	7.1
Unknown	—	50	17.1	10.7
Unknown	—	70	14.1	8.3
E_{max}			17.1	16.5

^a Courtesy of the Director of Geology and Mining, Dr. Enrique de Alba, Argentina.

^b Courtesy of Dr. P. Rouxhet, Laboratoire de Physico-Chimie Minérale, Haverlee-Louvain, Belgique.

As may be estimated from the data presented in Table 1, the E may be as large as E_{\max} , which corresponds to the conditions that $t_k \rightarrow 1$ and therefore $2t_k - 1 \rightarrow 1$. At $t_k = 1$ the membrane is ideal, *i.e.*, it is impermeable to ions of similar charge to that of the membrane, therefore it is impermeable to the whole electrolyte. Many of those samples that do show a potential, show the maximum possible potential for 10^{-4} M solutions, but all these samples have somewhat less than the maximum potential for the 10^{-3} solutions and this potential is at least 60 percent of the maximum potential. These data indicate that the pore size (radius) is of the same order as the thickness of the ionic atmosphere in the 10^{-4} to 10^{-3} M uni-univalent solutions: $305 \text{ \AA} - 96 \text{ \AA}$.

Not all muscovites possess the micropores responsible for the appearance of the membrane concentration potential. Several years ago Tschapek (1962) did not find the membrane concentration potential in one uncleaved muscovite sample (nearly 1 mm thick); Bean *et al.* (1970), using a similar procedure, did not find preexisting holes in muscovite sheets $5 \mu\text{m}$ thick. Although there is no direct relation between E and sheet thickness, most of the thinner sheets measured here show the presence of micropores. This fact means that the pores extend to hundreds and thousands and not to millions of primary sheets. It is interesting to note that all freshly cleaved samples possess the micropores responsible for the appearance of the measurable potential, whereas the uncleaved samples do not always give measurable potential. These facts are explainable by possible cracking even during very careful cleaving or by possible cracking during the natural weathering with time.

REFERENCES

- BEAN, C. P., M. W. DOYLE, AND G. ENTINE (1970) *J. Appl. Phys.* 41, 1454.
TSCHAPEK, M. (1962) *Z. Naturforsch.* 17b, 76.