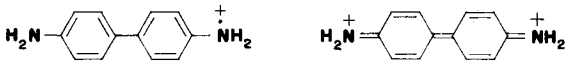
Clays and Clay Minerals, Vol. 24, pp. 51–52. Pergamon Press 1976. Printed in Great Britain

NOTE

ON THE MECHANISM OF STAINING MONTMORILLONITE BY BENZIDINE

The formation of benzidine-blue (monovalent semi-quinone—1.) and benzidine-yellow (divalent quinone—2.) by the reaction of benzidine with montmorillonite, has been discussed by several investigators (Furukawa and Brindley, 1973; Solomon *et al.*, 1968; Theng, 1971).



1 2

The benzidine-blue obtained in this way is strongly attached to the montmorillonite; it is very stable and may persist for several months. On the other hand, benzidine-blue formed in aqueous solution in the absence of clay, i.e. by the enzyme peroxidase, is unstable and is converted into benzidine-brown in a matter of a few seconds (Saunders, 1973; Lahav *et al.*, 1975). In the presence of montmorillonite, however, the benzidine-blue is stabilized. The blue color formed in aqueous solutions can be stabilized if treated with an expanding non-oxidizing clay mineral like hectorite (Furukawa and Brindley, 1973). Solomon *et al.* (1968) showed that the exchange cations have an influence on the color formation. The rate of formation is related to the ease with which the clay swells in water and hence the rate at which benzidine can penetrate to the inner layer regions. Solomon *et al.* (1968) have also shown by ESR measurements that iron in the crystal lattice of the montmorillonite is involved in the reaction. Therefore we believe that the stabilization of the colored radicals is the result of some kind of "short range" interaction between them and the oxygen sheets of the silicate layers.

It has been shown by Yariv and Lurie (1971) that π electrons of positively charged aromatic compounds (e.g. methylene blue) may interact with the oxygen sheet of montmorillonite. A similar interaction may take place between π electrons of the colored benzidine radicals and the clay oxygen sheet. Such an interaction can take place when the benzidine molecule approaches the oxygen sheet (penetration into the inner Helmholtz layer) and when the rings are parallel, or almost so, to the silicate layer.

We succeeded in extracting benzidine from montmorillonite by repeated washing of a benzidine–montmorillonite complex with organic solvents (ethanol, acetone and dioxane). The clay which was blue before washing lost its color. The supernatant organic solvent was colorless, presumably because of the instability of the radical.

The blue benzidine–montmorillonite had already lost its color through wetting with the organic solvent. However, the blue color reappeared upon drying. It reappeared also upon addition of NaCl. These observations are interpreted as indications that the 'short range' interaction between the aromatic ring and the oxygen sheet decreases in the presence of organic liquids, due to the solvation of the aromatic rings.

The possibility of penetrating of organic cations into the inner Helmholtz layer has been recently discussed by Yariv (1975). The probability for this penetration is given by the equation.

$$v = g \exp - [Z_i\psi + \Delta F_a + mF_s - \Delta F_d - \Delta F_n - \Delta F_p]/kT \quad (1)$$

where Z_i is the charge of the ion
ψ is the electric potential in this layer
$Z_i\psi$ is the 'long range' electrostatic attraction
g is a statistical factor which depends on the concentration of the organic ion
ΔF_a is the double layer association energy
ΔF_s is the 'short range' energy
ΔF_d is the dissociation energy of the micelles of the organic ions present in the aqueous solution
ΔF_n is the hydration energy of the organic ion in the aqueous solution
ΔF_p is the hydration energy of the clay
k is the Boltzmann constant
T is temperature.

The double layer association energy deserves further clarification. Water in the vicinity of the aromatic ring will have the 'hydrophobic hydration' structure. Thus repulsive forces acting on the aromatic ring are due to both the interaction of neighboring hydration water and the electric field emanating from the clay surface. Due to these repulsive forces in the double layer, the aromatic ring, as far as possible, will point away from the clay surface towards regions with lower electric field intensities. When the concentration of organic ions in the double layer increases, the possibility of hydrophobic moieties contacting each other will increase even if this requires that the distribution of the organic ions is inhomogeneous. By this contact, the amount of water having 'hydrophobic hydration' structure decreases and the result is a decrease of the repulsion forces between aromatic rings and the clay surface. Thus, associated benzidine molecules may reach the oxygen sheet and interact with this surface.

An increase of the fraction of associated benzidine molecules in the Helmholtz layer can be obtained by compressing the double layer. This can be done by increasing the electrolyte concentration. In order to do this, Na-montmorillonite suspensions with several NaCl concentrations were prepared at pH 7 (phosphate buffer) and the kinetics of benzidine-blue formation was measured

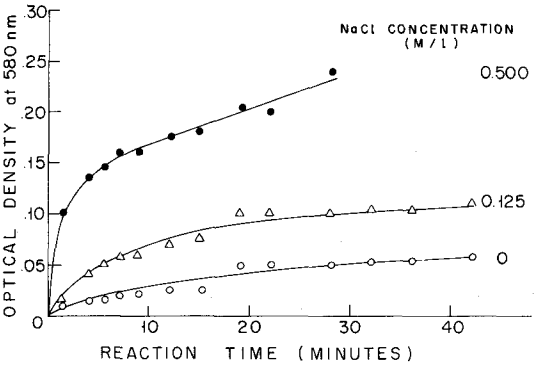


Fig. 1. Absorbance at 580 nm of clay–benzidine suspensions vs reaction time, at three NaCl concentrations: Na-montmorillonite—250 mg/l Benzidine concentration—25 ppm Phosphate buffer (pH 7)—0.021 M/l.

https://doi.org/10.1346/CCMN.1976.0240106 Published online by Cambridge University Press

with a Baush and Lomb spectrophotometer at wavelength 580 nm (Lahav and Raziel, 1971). The results are given in Fig. 1 where it is seen clearly that with increasing the salt concentration the development of the blue radical cation increases in both rate and amount.

The compression of the double layer can be also obtained by freezing (Anderson, 1967). We examined the effect of freezing on the minimum amount of benzidine required for the coloration of montmorillonite. Pastes of Na– and Ca–montmorillonite were mixed with various amounts of benzidine at decreasing weight ratios between benzidine and montmorillonite. It was found that the lowest ratio at room temperature was 0.00015 whereas in frozen montmorillonite–benzidine paste the lowest ratio was 0.00010. Although the lowest ratio depends also on the age of the clay, these two numbers can be used for comparative purposes.

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