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NOTE

Montmorillonite–Benzidine reactions in the frozen and dry states

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ON montmorillonite surfaces, the oxidation of the colorless benzidine molecule into the radical cation, benzidine-blue is ascribed to ferric ions occupying octahedral sites within the silicate layers and aluminum atoms in octahedral coordination exposed at the crystal edges. The evidence pertaining to this reaction recently was reviewed by Theng (1971) and by Lahav and Raziel (1971 a,b). As the hydrogen ion concentration in a montmorillonite-benzidine suspension increases, the blue color changes ultimately to yellow, with intermediate pale blue and pale pink in between (Lahav and Raziel, 1971b). The equilibrium between the blue monovalent semiquinone cation (B^+) and the yellow divalent semiquinone cation (Y^+) has been described (Dodd and Ray, 1960) as:

$$B^+ + H_3O^+ \rightleftarrows Y^{++} + H_2O. \qquad (1)$$

Dehydration of benzidine–montmorillonite system also results in a reversible color change from blue to yellow or yellow-green (Dodd and Ray, 1960; Kotov, 1955; Takahashi, 1955). This color reaction also has been attributed to a reduction in pH of the dried mineral surface (Solomon, 1968), since it has been established that clay surfaces become more acid as they dehydrate (Mortland *et al.*, 1963; Mortland and Raman, 1968; Touillaux *et al.*, 1968).

When a clay–water system is frozen only a portion of the water converts to ice; a significant amount remains unfrozen in a liquid or semi-liquid state. This unfrozen water forms a mobile surface layer that separates the mineral surfaces from those of the ice crystals. The thickness of the unfrozen, interfacial zone varies greatly with temperature: from 0 to about −5°C it ranges from 50 Å or more to about 9 Å; below −5°C and down to liquid nitrogen temperatures, the thickness diminishes from about 9 to about 3 Å (Anderson, 1967). As a rough generalization this seems to apply to all silicate minerals; however, there are important qualifications. For instance, in the case of the 2:1 expanding lattice clays, of which bentonite is a prominent representative, two distinctly different interfacial zones exist (Anderson and Tice, 1971 a,b). The precise nature of the distinction is not known, but one type may be associated with the planar surfaces whereas the other may be associated with curved menisci in interstices and convolutions of the pore space geometry. Alternatively, one type may be associated with the interlamellar water whereas the other type may be associated with the extralamellar layer of water that separates the clay tactoids from the enveloping ice. If the latter possibility is true, it seems that the extralamellar interfacial water layer must be the thicker of the two (Anderson and Tice, 1971 a,b).

Freezing of a clay–water system, in effect, is analogous to drying it. In both cases water is removed, concentrating the solutes, bringing about the formation of complexes and perhaps inducing precipitation in the remaining interfacial liquid. Consequently, it is to be expected that the color changes in a montmorillonite–benzidine system during freeze–thaw cycles will be similar to that observed during hydration–dehydration cycles. In this note we present the observations that confirm this view.

Three preparations of Fisher bentonite B-235 were used; (a) Raw clay mineral without any pretreatment; (b) Na–bentonite; and (c) Ca–bentonite. The latter two were of size fractions smaller than 2μm e.d. as described elsewhere (Banin and Lahav, 1968). Umiat bentonite in the Cu-form was also used in the present study.

In each of the above bentonites a series of suspensions or pastes was prepared in whcih the benzidine/bentonite ratio (W/W) was varied over a wide range. In the raw bentonite, the clay and benzidine (May and Baker) powders were mixed and water was then added. The pastes or suspensions were mixed or shaken and left standing with occasional shaking for more than two weeks to insure that stable colors had developed before the first experiment was performed. In all the other preparations benzidine solutions were added to the clay suspensions at the desired rate.

Most of our observations were made at −15 and −21°C but several observations were made at −5, −80°C and liquid air temperature. Samples from each preparation were transferred into a test tube, stoppered and brought to a desired temperature. The color changes were noted by comparing visually each of the frozen suspensions with a corresponding one that was kept at room temperature, or a previously frozen one that had been thawed. X-ray study was carried out in the raw bentonite series. Samples of the bentonite-benzidine pastes were dried at 25°C and then repulverized. The powders were left standing for one more week at 25°C and about the same relative humidity before being subjected to X-ray diffraction. The 001 spacing of the bentonite-benzidine powders was measured according to the method of Barshad (1960).

At −5°C no color changes were observed in any of the frozen bentonite–benzidine–water mixtures. At −15°C and −21°C, however, distinctive color changes on freezing were apparent in *all* the bentonites under study when the benzidine/bentonite ratios were between approximately 0·0003 and 0·003 (W/W). The color changed from blue or gray–blue to green or bluish green; the process was reversible on thawing and practically independent of water content from 7 gm water/gm clay to 130 gm water/gm clay.

At benzidine/bentonite ratios lower than about 0·0003

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the pale color of both the frozen and unfrozen clay was virtually indistinguishable from that of a pure bentonite-water system, whereas at ratios higher than about 0·003 the deep blue color of the frozen clay–benzidine persisted after freezing and no change could be observed at −21°C for several months or at −180°C for several hours. In the treatments where color changes were observed to occur, the changes were similar to those observed during dehydration of benzidine–bentonite pastes (Lahav, 1972).

Table 1 summarizes the observations for the raw bentonite. Very similar patterns of color change were found also for all the other bentonite preparations.

Table 1. Color and 001 spacing of the benzidine–bentonite systems

g benzidine g bentonite	Paste water content (g water/g/bentonite)	001 spacing of air-dry powder (Å)	Color Paste	Air-dry	Frozen
Control (no benzidine)	10	13·2	Gray–yellow	Gray–yellow	Gray–yellow
0·0002	10	13·1	Gray–yellow	Gray–yellow	Gray–yellow
0·0002	7	13·1	Gray–yellow	Gray–yellow	Gray–yellow
0·0022	10	12·5	Blue	Green–yellow	Yellowish green
0·0022	7	12·2	Blue	Green–yellow	Yellowish green
0·011	10	14·7	Blue	Gray–blue	Blue
0·22	2	14·7	Deep blue	Gray–blue	Deep blue
0·22*	2	15·0	Dark blue	Dark	Dark blue

*The dry powders of the bentonite and the benzidine were mixed and left for two months in the laboratory before adding water. Dark blue color formation started in the air-dry mixture.

Reflectance measurements of bentonite-benzidine systems in the air dry state and in paste (Lahav, 1972) indicate that the green or bluish green colors probably result from a combination of blue and yellow forms which coexist at the clay surface. The results of freezing and dehydration are similar, but in the case of freezing, the color change does not go beyond green whereas during drying, the color may go to yellow, depending on both the benzidine–bentonite ratio and the air relative humidity (Lahav, 1972). This difference obviously results from the fact that it is possible to carry dehydration virtually to completion whereas in the frozen systems under study, an unfrozen, liquid interface of finite thickness is always present, even at the lowest temperatures.

At low surface concentrations the benzidine molecules are expected to lie in such a way as to present their minimum thickness, whereas at high surface concentration most of the benzidine molecules are thought to orient such that planes are perpendicular to the planes of the silicate sheet. Thus, the 001 spacing should be about 12·5 and 15·2 Å for the low and high surface concentration, respectively (Greene-Kelley, 1955). The 001 spacings of 14·7 and 15·0 Å (Table 1) are somewhat smaller than the ones observed by Takahashi (1955) and Greene-Kelley (1955) but seem to fit the model proposed by the latter. More experimental data are needed for a detailed description of the system at low benzidine concentrations but it should be noted that if each benzidine molecule in the air-dried system underwent oxidation and formed a monovalent cation, these cations would constitute about 1 per cent of the C.E.C. at the benzidine/bentonite ratio of 0·002. Therefore, at this low concentration, all the benzidine molecules could have been sorbed on the crystal edges. Since the measured 001 spacing of 12·2–13·1 Å (Table 1) can result from the presence in the interlamellar space of either water molecules alone or both molecular species, present data do not distinguish between the two possible sites for benzidine sorption.

By replacing some of the exchangeable metal cations from the clay surface (Dodd and Ray, 1960; Lahav and Raziel, 1971), the sorbed benzidine molecules decrease the surface acidity by reducing the polarization of the sorbed water ordinarily caused by exchangeable metal cations (Mortland *et al.*, 1963; Touillaux *et al.*, 1968; Mortland and Raman, 1968). In this fashion we can explain the dependence of the color change of the air-dried benzidine–bentonite system on both the relative humidity and the benzidine concentration (Lahav, 1972) and the observation that at the high benzidine concentration the transformation of the blue form into the yellow one is only partial even under extreme dehydration conditions.

The color changes brought about by freezing indicate that as a result of the decrease in the thickness of the liquid films on the clay surface, there is an increase in the degree of dissociation of the water molecules similar to that taking place upon dehydration. However, the change of the blue form to yellow is incomplete as evidenced by the resulting green color of the frozen pastes. The simultaneous existence of the two forms, even under extremely low temperatures, must result from the inhomogeneity in the system. This inhomogeneity can be viewed either as a nonumiform distribution of benzidine molecules during preparation of the specimens or as the existence of distinctly different regions on the clay surface having different sorption and electron-transfer capacities. The color reaction took place in all the clays under study with two different methods of preparation. Thus, the inhomogeneity results from an intrinsic property of the system: the planar surfaces and the crystal edges must have distinctly different sorption and acidic characteristics. Moreover, the mode of association of the unit layers into particles, or tactoids, creates two types of planar surfaces, namely internal and external regions. Finally, at the low benzidine/bentonite ratios (where color change does take place), freezing of the bentonite–water–benzidine system brings about lattice collapse and a decrease of the initial 001 spacings (Anderson, 1967). In the thin inter-

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lamellar liquid film the equilibrium between the adsorbed Y^+ and B^+ forms is shifted toward the formation of Y^+, whereas on the external surfaces the film thickness is greater and the blue form is predominant. The combination of the blue and yellow gives the green hues. Any or all of these circumstances help account for the results.

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