The Effect of Layered Water on the Color Reaction of Benzidine or Other Similar Compounds with Montmorillonite

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Introduction

It is well known that certain clay minerals form stable complexes with some organic compounds. Complexes between montmorillonite and aromatic amines are particularly well known, because of their deep colors.[1,2] Investigations on the structure of the complexes as well as their color reactions have been reported by several authors. It has been clarified[3,4,5] through the X-ray diffraction method, that in these complexes organic molecules lie along can be held between two adjacent sheets of successive silicate layers, generally as a single layer or double layers just similar to the behavior of water molecules in natural montmorillonite. A schematic illustration of a montmorillonite complex after Hendricks and Jefferson[4,6] is shown in Fig. 1.

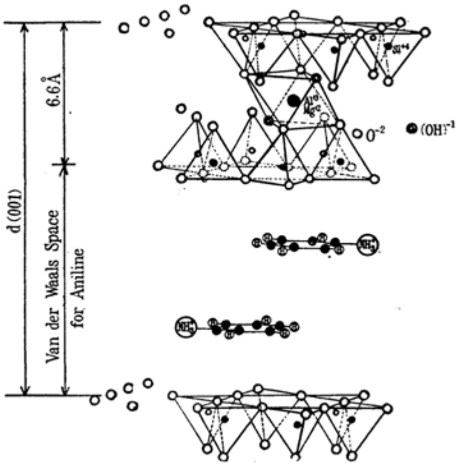

Fig. 1. Schematic drawing showing organic molecules between silicate layers of montmorillonite after Hendricks and Jefferson.

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[1] K. Kobayashi and K. Yamamoto, *J. Soc. Chem. Ind. Japan*, **26**, 289 (1921).

[2] E. A. Hauser and M. B. Leggett, *J. Am. Chem. Soc.*, **62**, 1811 (1940).

[3] J. B. Gieseking, *Soil Sci.*, **47**, 1 (1941).

[4] S. B. Hendricks, *J. Phys. Chem.*, **45**, 65 (1941).

[5] D. M. C. MacEwan, *Trans. Farad. Soc.*, **44**, 349 (1948).

[6] S. B. Hendricks and M. E. Jefferson, *Am. Mineral.*, **23**, 863 (1938).

In regard to the mechanism of the coloration displayed in the complex between montmorillonite and benzidine, Kameyama and Oka⁷⁾ have assumed that the benzidine molecule is colored in the semiquinone form due to the oxidation by the manganese ion which is present in clay as impurity, while, Weil-Malherbe and Weiss⁸⁾ ascribed it to the oxidation by the ferric ion present in the octahedral layer of the clay mineral. The present author, however, has found that the coloration is influenced remarkably by the amount of the absorbed water, i.e., interlayer water which is present between the adjacent silicate layers.⁹,¹⁰⁾ From this point of view, the present article will report on the mechanism of the formation of complexes as well as the color reactions between some montmorillonite and benzidine or some related compounds, discussing them in comparison with each other.

Clay Samples.—The clays used in this experiment are Wyoming bentonite, Bodai acid clay and Numata clay, from Osage, Wyoming, U.S.A., Bodai, Naya-mura, Ishikawa Prefecture and Shimokawada, Kawada-mura, Gunma Prefecture, respectively. The refined samples have been obtained from these clays after having thoroughly elutriated them in the usual way. The X-ray powder patterns of these samples have shown that they have montmorillonite for the main ingredient.¹¹⁾ Bodai acid clay alone, however, contains α-cristobalite and quartz as impurities. (Cf. Table I) Their differential thermal analysis curves (Fig. 2) reveal that they are montmorillonite type, and the rate of heating is 12°C per minute.¹²⁾ In this figure, however, Numata clay alone has an endothermic peak at 560°C, which may be due to the possible presence of illite or kaolin minerals as an impurity in Numata clay,¹³⁾ though its presence has not yet been found in the X-ray powder pattern.

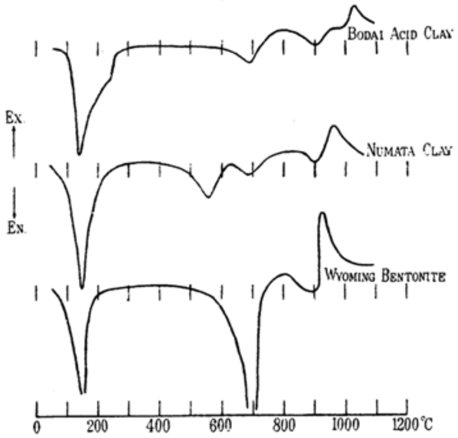

Fig. 2. Differential thermal analysis curves of clay samples.

The chemical formulas¹⁴,¹⁵⁾ obtained from the chemical analysis of these clay samples, all of which are assumed as montmorillonite, are given below:

Wyoming bentonite:

$$(Al_{1.50}Fe_{.18}Mg_{.32})\ (Al_{.01}Si_{3.99})O_{10}(OH)_2X^{I}{}_{.33}$$

Bodai acid clay:

TABLE I

THE X-RAY POWDER PATTERNS OF CLAY SAMPLES

Indices	Bodai acid clay		Numata clay		Wyoming bentonite	
	d	*I*	*d*	*I*	*d*	*I*
001	15.4	10	15.4	10	15.4	10
003	5.14	2	5.15	1	5.16	1
02,11	4.46	6	4.50	5	4.51	5
	4.21 (Q)					
	4.04 (α-C)					
	3.35 (Q)					
005	3.09	2	3.05	1	3.07	2
13,20	2.56	3	2.57	2	2.58	2
31,15,24	1.72	0.5	1.69	0.5	1.70	0.5
33,06	1.498	3	1.496	2	1.500	3

Key to abbreviations: d=spacing in kx, I=intensity, Q=quartz pattern, α–C=α–cristobalite pattern

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7) N. Kameyama and S. Oka, *J. Soc. Chem. Ind. Japan*, **32**, 294 (1929).

8) H. Weil-Malherbe and J. Weiss, *J. Chem. Soc.*, **1948**, 2164.

9) S.B. Hendricks, R.A. Nelson and L.T. Alexander, *J. Am. Chem. Soc.*, **62**, 1457 (1940).

10) J. Mering, *Trans. Farad. Soc.*, **42-B**, 205 (1946).

11) D.M.C. MacEwan, "X-ray Identification and Crystal Structures of Clay Minerals", edited by G.W. Brindley, The Mineralogical Society (Clay Mineral Group). London, (1951) p. 124.

12) R.E. Grim, "Clay Mineralogy", McGraw-Hill Book Co., Inc., New York, N.Y., (1953), p. 197.

13) T. Sudo et al., *J. Geol. Soc. Japan*, **58**, 115 (1952).

14) C.S. Ross and S.B. Hendricks, *U.S. Geol. Surv. Bull.*, Prof. Paper, **205-B**, 23 (1945).

15) Y. Otsubo, "Chemical Researches, No. 8", Asakura Book Co., Tokyo, (1950), p. 85.

$(Al_{1\cdot64}Fe_{\cdot15}Mg_{\cdot32})\ (Al_{\cdot13}Si_{3\cdot87})O_{10}(OH)_2X^{I}{}_{\cdot34}$

Numata clay:

$(Al_{1\cdot55}Fe_{\cdot16}Mg_{\cdot33})\ (Al_{\cdot08}Si_{3\cdot92})O_{10}(OH)_2X^{I}{}_{\cdot29}$

Exchangeable cation is sodium in Wyoming bentonite and Numata clay, while it may be both sodium and calcium in Bodai acid clay. However, as it may be considered to have the least effect on the color reaction of complexes, further discussion on cation exchange seems to be unnecessary for the present purpose.

Of the plate type and fluffy type which usually characterize the shape of montmorillonite, these clays are considered to belong to the latter type, from the electron micrographs of them.[16,17,18)

As a result of all the experiments above, it seems to be certain that these clay samples are montmorillonite.

Preparation of Specimens.—Complexes between montmorillonite and every one of the following organic substances such as benzidine, γ-diphenol, aniline, phenol, *p*-phenylenediamine and monomethyl-*p*-aminophenol were prepared for the present investigation. To prepare a complex, the water-alcohol solution of a given organic compound is poured into an aqueous suspension of clay. The amount of the organic compound which is added is as much as several times the base exchange capacity of the clay (5–10 milliequivalent per one gram of clay). The suspension of the complex thus prepared was centrifuged after left over twenty four hours. The precipitates obtained were washed with alcohol and water repeatedly until free compounds were no longer present, and dried in air. From every kind of these air dried complexes, four kinds of specimens were made by the following processes:

(1) Absorption of water by standing in the saturated water vapor at 20°C for about a week,

(2) complete absorption of water by direct wetting,

(3) dehydration by standing over phosphorus pentoxide,

(4) absorption of water by wetting again after (3) procedure was applied.

The specimens prepared by these processes will hereinafter be abbreviated as S-1, S-2, S-3 and S-4 for every complex.

Experimental and Discussion

It was found that the color of the complex is varied remarkably, in some cases, accordingly to the way of preparation of the specimen, and in other cases, it is not. The colors of specimens of each complex are shown in Table II, along with the values of their (001) spacings obtained by a Philips X-ray Geiger counter spectrometer. Filtered copper radiation, 35 Kv, 15 Ma, scan speeds 2° and 1/2° per minute, angular aperture 1°, receiving slit 0.006 inch, time constant 4 second.

TABLE II

THE (001) SPACINGS AND THE COLORS OF THE SPECIMENS FOR EACH COMPLEX

		Bodai acid clay	Numata clay	Wyoming bentonite	color
benzidine	S-1	15.4 kx	15.4	15.3	blue
	S-2	19	19	19	blue
	S-3	13.8	13.9	13.2	yellow∼colorless
	S-4	19	19	19	blue
γ-diphenol	S-1	16.1			green
	S-2	19.5			green
	S-3	14.7			colorless
	S-4	19.5			green
aniline	S-1	15.3	15.2	15.2	very light violet
	S-2	18	18	19	very light violet
	S-3	13.5	13.5	12·4	very light violet∼colorless
	S-4	18	18	19	very light violet
phenol	S-1	15.2	15.2	15.2	colorless
	S-2	18	19	18.5	colorless
	S-3	14.5	14.5	13.4	colorless
	S-4	19	18	18.5	colorless
p-phenylene diamine	S-1	15.4	15.4	15.4	violet (blue)
	S-2	15.4	15.4	15.4	violet
	S-3	15.2	14.5	14.7	violet
	S-4	15.4	15.4	15.4	violet
mono-methyl -*p*-amino phenol	S-1	15.4	15.3	15.3	violet (light green)
	S-2	15.4	15.3	15.4	violet
	S-3	15.1	13.3	14.0	violet
	S-4	15.4	15.2	15.4	violet

With respect to the benzidine complex, Table II reveals that the color reaction is caused by the presence of water and when dehydrated as S-3 the color can not be developed. The color of the air dried complex when it is further dried over calcium chloride becomes yellowish green and the (001) spacing is 14.5–15.0 kx. The yellowish green color gradually turns to blue when the complex is in equilibrium with water vapor, and

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16) R.P. Humbert and B.T. Shaw, *Soil Sci.*, 52, 481 (1941).

17) B.T. Shaw, *J. Phys. Chem.*, 46, 1032 (1942).

18) P.F. Kerr et al., "API Report Project 49", No. 6 (1950).

TABLE III

THE VARIATION OF (001) SPACINGS OF CLAYS AND THEIR BENZIDINE COMPLEXES WITH THE ABSORPTION OF WATER

	Bodai acid clay		Numata clay		Wyoming bentonite	
	natural clay	complex	natural clay	complex	natural clay	complex
absorbed water vapor	15.4 kx	15.4	15.4	15.4	15.4	15.3
saturated with water	19	19	19	19		19
dried over $CaCl_2$	13.6	14.8	13.7	14.9	13.3	14.5
dried over P_2O_5	12.4	13.8	12.4	13.9	12.0	13.2

the (001) spacing becomes equal to the value of S-1. It is inferred from this fact that, in the case of the benzidine complex, the color varies, depending on the amount of water held between two neighbouring sheets of successive silicate layers.

Table III shows the variation of the (001) spacings of the clay samples with the absorption of water, in comparison with their benzidine complexes. The (001) spacing of natural clays are 15.4 kx when they are in equilibrium with water vapor. This implies that they have two water layers between two adjacent silicate layers. When the clays are saturated with water, they swell and in the case of Bodai acid clay and Numata clay, the (001) spacing increases to 19 kx, which corresponds to the increment of one or two water layers, whereas, in Wyoming bentonite, the (001) spacing becomes too large to estimate its value. When benzidine complex is saturated with water, the increment in the number of water layers is one or two, just as in the case of natural Bodai and Numata clay. As well as in the case of Wyoming bentonite; it is of interest to note that it can not swell so much as in the natural state when it forms a complex.

Table III shows also that even in the dehydrated state there still remain the benzidine molecules themselves between the silicate layers. Therefore, decoloration is caused, not by the absence of benzidine molecules themselves, but by the absence of water.

The presence of the layered water is necessary for the color reaction; moreover, it was found that some liquids other than water also show the same effect. For the purpose of estimating the absorbed water thoroughly, the clay was heated to 300–400°C. That the layered water is no longer present in it, is demonstrated by its X-ray diffraction diagram, by which, its (001) spacing was found to be 9.5 kx. When a water solution, an alcohol solution and an acetone solution of benzidine were added to the dehydrated clay respectively, it was found that the color of the complex became blue, greenish blue and yellow according to the solvent. This fact means that the color reaction of this complex changes according to the kind of liquid which is present between layers.

The same effect is also demonstrated in the following way. When water, alcohol and acetone are added respectively to a benzidine complex which has been dehydrated thoroughly to a colorless state, it becomes blue, greenish blue and yellow respectively as above. In this case, however, if benzene is added to the complex, the appearence of color can not be observed.

γ-diphenol whose construction approximates to benzidine, shows similar behavior in the formation of complex with these clays. However, amino-radical has a greater effect of deepening the color of the complex than in the case of hydroxyl-radical as revealed from Table II.

p-Phenylenediamine(paramine)-montmorillonite and monomethyl-*p*-aminophenol(methol)-montmorillonite complexes have deep colors, which do not change even when they are dried, in contrast with the case of benzidine or γ-diphenol complex. It is worthy to note that there is no difference in the value of (001) spacing between S-2 and S-3 (the dried state and the water saturated state). It is presumably because of the fact that these complexes in themselves have little layered water, and even when they are dried or saturated with water, it dose not affect the quantity of the layered water in them. What deserves particular attention here is the fact that, in the paramine and methol complexes, their colors are blue and green respectively when they are made freshly in the clay suspension, and then these colors change to violet as time passes or if they are dehydrated. This fact may lead to an assumption that in the first stage of the formation, these complexes temporarily make benzidine-like coloration, but in the next stage their colors change as the molecules of paramine or methol fix on both sides of the silicate layers, no longer permitting the water molecules to get into them. It is, however, ascertained through X-rays that in the case where the quantity of paramine and of methol is not saturated, the shrinkage or swelling occurs to some extent of movement of the water getting into or out of them.

In contrast with paramine and methol, the coloration of the aniline complex is not so remarkable. In the case of phenol, which is believed to be able to form a complex with montmorillonite,[2,5] the coloration can not be recognized by the naked eye. This unremarkable coloration is due to the fact that aniline and phenol are monofunctional compounds, and the amino- or hydroxyl-radical fixes on one side of the silicate layer. When these complexes are saturated with water, the increment in the number of water layers is one or two just as in the case of benzidine complex.

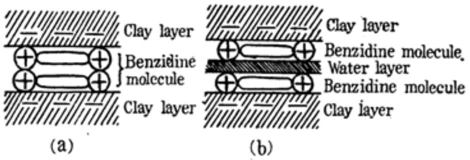

Fig 3. The process of benzidine complex formation with montmorillonite.
(a) Complex is formed.
(b) Saturated with water.

The benzidine and paramine complexes show a remarkable coloration, as they are bifunctional compounds. In the case of the benzidine complex, a benzidine molecule fixes on one side of the silicate layer, and then when it is saturated with water, the water molecules get into the silicate layer. From this fact, a schematic drawing of the process of benzidine complex formation with montmorillonite is shown in Fig. 3.

Summary

The relationship between layered water and coloration of some complexes between montmorillonite and benzidine or other similar compounds has been discussed, and it is shown that they may be divided into types according to the structures of organic compounds. The shrinkage and swelling of the layer distance of the complex caused by its dehydration and hydration are observed.

The coloration of the monofunctional-complex is not so remarkable and that of the bifunctional-complex is remarkable. In the case of monofunctional-complex or the bifunctional-complex with benzidine, the amino- or hydroxyl-radical fixes on one side of the silicate layer, and then, when it is saturated with water, the water molecules get into the silicate layer. On the other hand, in the bifunctional-complex with paramine, as the amino- or hydroxyl-radical fixes on both sides of the silicate layers, the water molecules no longer get into it.

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