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Diffuse Reflection Spectra of Acid Clays Colored with Benzidine and Some Other Diamines

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In order to identify the species responsible for the coloration of acid clay upon the addition of benzidine and related aromatic diamines, the diffuse reflection spectra of colored clays in the presence of water, methanol, and benzene were examined in the range from 4 to 29 kK. The coloration appeared to be due to the oxidation of the diamines held between the silicate sheets to the mono- and di-valent cations. The former cations were found to be in various modes of intermolecular interaction, depending on the kind and amount of the liquid. The lightening of the color upon drying was attributed to the disproportionation of the monovalent cations to the divalent cation and the protonated molecule.

It has been known that the addition of benzidine and other aromatic diamines to some clay minerals produces deep colors.[1,2] Examining the absorption spectra of acid clays suspended in benzene and colored by benzidine and its tetramethyl derivative, Hasegawa has concluded that the quinoidal and meriquinoidal forms of the diamines are responsible for the coloration.[3] In recent years much knowledge of the electronic spectra of ion radicals, including those derived from the diamines, has accumulated. It is now clear that the electronic spectra depend considerably on the mode of aggregation, *e.g.*, monomeric, dimeric or polymeric. Even in the solid state the presence of various modes of intermolecular interactions has been pointed out on the basis of the spectra.[4] As the diamine molecules held between the silicate sheets are in the form of a double layer,[5] it is not likely that the cation radicals in colored clays are free from intermolecular interaction. Therefore, no complete identification of the colored species in acid clays as the monovalent cations can be made without considering the mode of aggregation. In addition, a lightening of the colors on drying and a deepening on wetting have been noted by Hauser and Leggett and also by Takahashi.[2,5] To measure the spectral changes in such processes it seemed to us that the method of diffuse reflection has great advantages.

Experimental

Materials. The acid clay supplied by Wako Pure Chemical Industries, Ltd., was refined by repeated elutriations. Colored clays were prepared by mixing a diamine dissolved in a suitable organic solvent and the clay suspended in the same; the mixture was then filtered and washed throughly with the solvent. The samples thus prepared were quickly dried in a vacuum and then moistened with the liquid selected for the spectral measurements. For example, a 0.37-g portion of benzidine dissolved in 20 m*l* of methanol was added to 3.0 g of the clay suspended in 20 m*l* of methanol. The color was blue, but it turned green and finally yellow on drying. The carbon content of the dried sample was found by elemental analysis to be 1.48%, corresponding to a benzidine content of 1.89%. The diamines and the solvents used for sample preparations were as follows: benzidine in methanol, *o*-tolidine in methanol, *N,N,N′,N′*-tetramethylbenzidine in benzene, and 1,6-diaminopyrene in acetone. The cation radical salts of the first three diamines were prepared according to the methods of Hughes and Hush.[6] The solid bromides of the mono- and di-valent 1,6-diaminopyrene cations were made by the oxidation of the diamine dissolved in xylene with bromine, as has been described by Scott *et al.*[7]

Measurements. The difference in reflectance between a colored clay and the dry refined acid clay was recorded by means of a Beckman DK 2A spectroreflectometer. The spectra were plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. The function is supposed to be equal to the absorption coefficient divided by the scattering coefficient. As both the coefficients are affected by the pres-

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1) K. Kobayashi and K. Yamamoto, *Kogyo Kagaku Zasshi*, **26**, 289 (1921).

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

3) H. Hasegawa, *J. Phys. Chem.*, **65**, 292 (1961).

4) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

5) H. Takahashi, *ibid.*, **28**, 5 (1955).

6) G. K. Hughes and N. S. Hush, *J. Proc. Roy. Soc. N. S. W.*, **81**, 48 (1947).

7) H. Scott, P. L. Kronick, P. Chairge and M. M. Labes, *J. Phys. Chem.*, **69**, 1740 (1965).

ence of a liquid, we must seek a set of conditions such that the change in the absorption coefficient is of major importance in determining the change in the spectra. When colored clays are only slightly moistened, *e.g.*, by a few drops of liquid per gram of the clay, the spectra were found to be approximately comparable with each other. The procedures used for the spectral measurements of the solid ion-radical salts were described in an earlier paper.[4]

Results

Benzidine-acid Clay. The dried sample is yellow, and the spectrum has only one absorption maximum, located at 22.5 kK. As is shown in Fig. 1, a weak, continuous absorption can be seen in the low-energy region if the sample is not quite dry. On slight moistening with water, the absorption in the low-energy region is intensified and that at 22.5 kK is considerably weakened. The presence of maxima at 9.5 and 14.5 kK and a shoulder at 16 kK can be clearly noted. (Hereafter this will be called the pattern B-2). The further addition of water to the sample modifies the spectrum drastically. The absorption at 22.5 kK almost decays out, and absorption maxima at 7.5, 12.0, 17.0, and about 27 kK form the pattern B-1. When the sample is very wet, the pattern remains the same as the pattern B-1, but the intensities may be hundreds of times higher than those shown in Fig. 1.

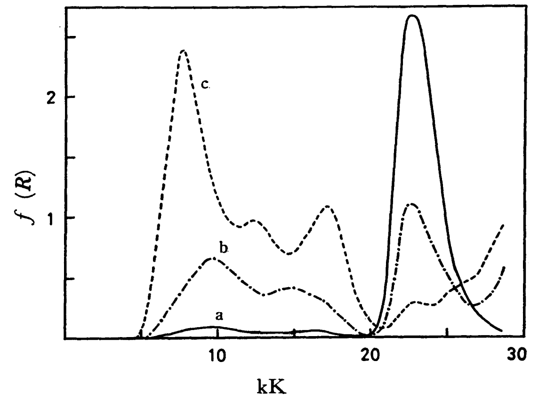

Fig. 1. Diffuse reflection spectra of benzidine-acid clays moistened with water; (a) nearly completely dried, (b) moistened, (c) moistened further.

The spectra of the samples moistened with methanol are shown in Fig. 2. The pattern B-2 can be more clearly observed here than in the clays moistened with water. An absorption maximum now clearly appearing at 26 kK is considered to be a part of this pattern. This figure presents a good example of how the spectral change by the addition of a liquid is reversible. A slightly moistened sample was examined first (curve a). Then the sample was nearly completely dried (curve b), and finally it was moistened again with methanol (curve c). The pattern B-1 can be observed in this combination, too, provided that the samples are soaking wet.

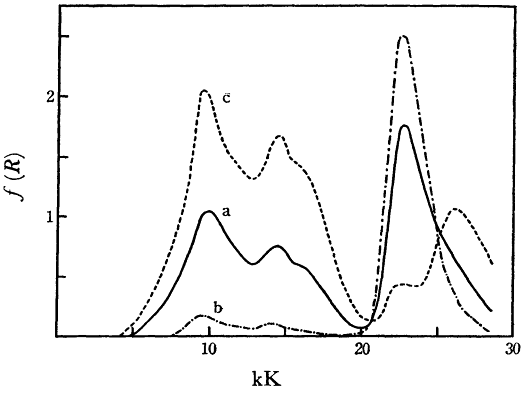

Fig. 2. Diffuse reflection spectra of benzidine-acid clays moistened with methanol; (a) moistened, (b) nearly completely dried, (c) moistened again.

Moistening the dried samples with benzene results in the appearance of a spectrum entirely different from that described above. The pattern B-3, found in Fig. 3, consists of absorption maxima at 11.5, 15.2, and somewhere around 27 kK.

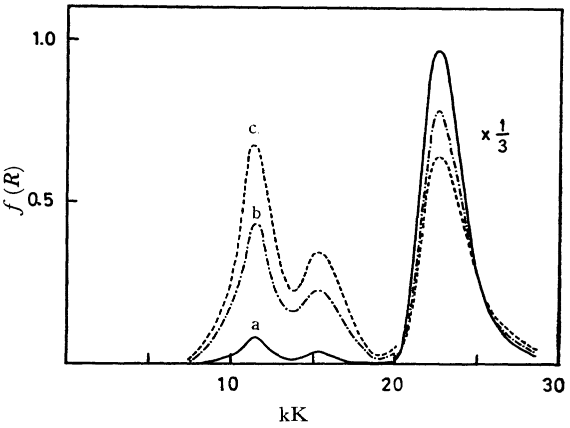

Fig. 3. Diffuse reflection spectra of benzidine-acid clays moistened with benzene; (a) nearly completely dried, (b) moistened, (c) moistened further.

The results given in Figs. 1, 2, and 3 were all obtained using freshly-prepared samples. On storage the absorption at 22.5 kK is slowly intensified and the sample becomes less sensitive to moisture. Long after preparation, the deep color does not develop on either moistening or soaking.

***o*-Tolidine-acid Clay.** In this system the samples moistened with methanol show essentially the same spectra as those moistened with water. Figure 4

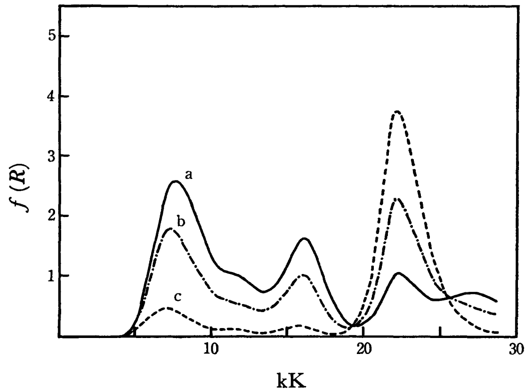

Fig. 4. Diffuse reflection spectra of *o*-tolidine-acid clays moistened with methanol; (a) moistened, (b) moistened less, (c) nearly completely dried.

presents the spectra obtained by the former combination. The pattern T-1 characteristic of the deep-colored clays consists of absorption maxima at 7.5, 16.0, and 27.0 kK and a shoulder at 11.5 kK; it bears a close resemblance to the pattern B-1.

On moistening with benzene absorption maxima are observed at 10.7, 14.5, and 27 kK. The pattern shown in Fig. 5 may be designated as T-3 because of its similarity to the pattern B-3. It should be noted that the spectra given in Figs. 4 and 5 were taken in the process of drying.

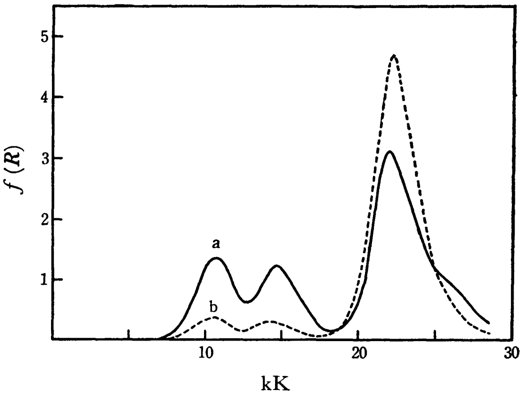

Fig. 5. Diffuse reflection spectra of *o*-tolidine-acid clays moistened with benzene; (a) moistened, (b) nearly completely dried.

Tetramethylbenzidine-acid Clay. The sample prepared in benzene is green. This color lightens only very slowly on drying. The spectrum (curve a) given in Fig. 6 was obtained after three weeks' storage over silica gel. By the addition of methanol, the absorptions at 7—7.5, 14—14.5, and 25 kK are intensified. The spectrum exhibited by the moistest sample in the figure (curve c) is practically the same as that exhibited by the sample freshly prepared in benzene.

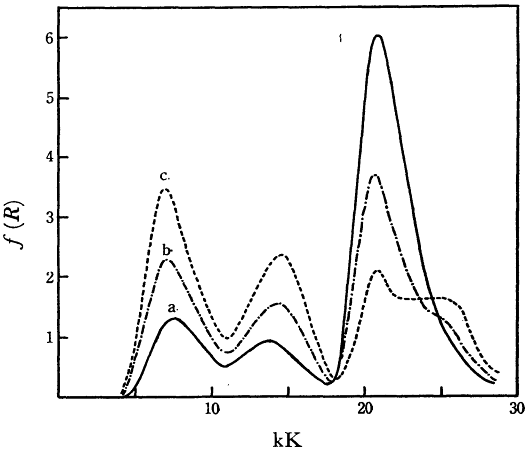

Fig. 6. Diffuse reflection spectra of tetramethylbenzidine-acid clays moistened with methanol; (a) nearly completely dried, (b) moistened, (c) moistened further.

Diaminopyrene-acid Clay. The freshly-prepared sample is dark brown. The color turns to a reddish brown on standing. As is shown in Fig. 7, the disappearance of absorptions at 6.5, 14.7 and about 26 kK is the cause of this color change. As grinding and moistening accelerate this change, the effects of the added liquid cannot be ascertained.

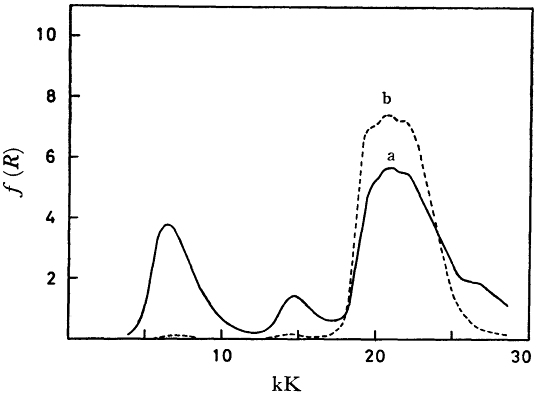

Fig. 7. Diffuse reflection spectra of dry diaminopyrene-acid clays; (a) freshly prepared, (b) stored for three days.

Bromides of Mono- and Di-valent Cations. The spectra of the cation radical salts derived from benzidine and its tetramethyl derivative were described in a previous paper.[4] The bromide of the monovalent *o*-tolidine cation gives a spectrum very similar to them. The locations of the absorption maxima are as follows: 6.8, 15.5, and 26.0 kK in the benzidine bromide, 7.5, 16.0, and 27.0 kK and a shoulder at 11.5 kK in the *o*-tolidine bromide, and 8.0, 14.7, and 25.0 kK in the tetramethylbenzidine bromide.

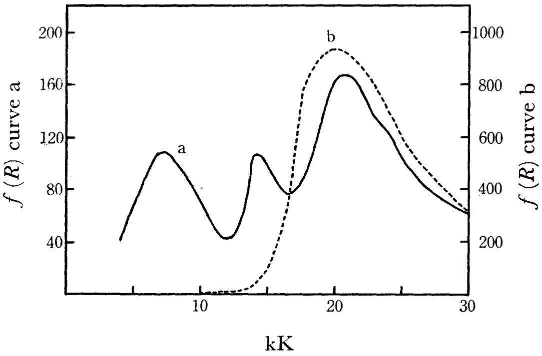

Fig. 8. Diffuse reflection spectra of diaminopyrene bromides; (a) monobromide, (b) dibromide.

The bromides of mono- and di-valent diaminopyrene cations show the spectra given in Fig. 8. It must be added that the intensity of the absorption near 20 kK in the dibromide is about five times stronger than that in the monobromide. In addition to a broad absorption appearing around 21 kK, the monobromide exhibits absorption maxima at 7.0 and 14.0 kK.

Discussion

First of all we must note that none of the spectra of the colored clays studied here exhibits a pattern which can be assigned to the monomeric form of the cation radicals. The patterns B-1 and T-1 and that in the spectra of the clay colored with tetramethylbenzidine resemble those of the solid bromides. Furthermore, the pattern B-3 is close to that of the dimeric cation radicals in solution. The latter is known to consist of absorption maxima at 12.4, 16.4, and 27.8 kK.[8] Perhaps only the cation radicals can show such pronounced variations and coincidence of the spectra. Therefore, the patterns B-1 and T-1 and that in the spectra of the clays colored with tetramethylbenzidine may be assigned to the univalent diamine cations in more-than-by-pairs interactions, while the patterns B-3 and T-3 may be assigned to the cations in pair-by-pair interactions. The presence of the pattern B-2 indicates that there is another mode of more-than-by-pairs interaction in this particular case.

The absorption spectra of the acid clays colored with benzidine and with its tetramethyl derivative reported by Hasegawa[3] are in agreement with those we give in Fig. 3 (pattern B-3) and Fig. 6 respectively. Although the monovalent cations, Hasegawa's meriquinoidal forms, are responsible for the deep colors developed in these two systems, it must be pointed out that the cations are in different modes of intermolecular interaction.

Hasegawa has reported that the quinoidal form, presumably the divalent cation in our nomenclature, of tetramethylbenzidine dissolved in ethanol exhibits an absorption at 21.3 kK. The absorption at 20.8 kK in Fig. 6 may be assigned to this species. We may conclude that the species giving strong absorptions in the range between 20 and 23 kK of Figs. 1—5 are also the divalent diamine cations. This conclusion is in accordance with the observation that these absorptions are slowly intensified on storage until finally these are the only ones to be detected.

1,6-Diaminopyrene has been known to form solid bromides of the mono- and di-valent cations.[7] The spectra in Fig. 8 may well be compared to those of the clays colored with this diamine in Fig. 7. The freshly-prepared sample shows the pattern characteristic of the monobromide, but after three days' storage only the absorption to be assigned to the dibromide can be observed. These findings are consistent with our observations concerning the clays colored with benzidine and its derivatives.

As has been mentioned before, the spectra in each figure from 2—6 are only approximately in the same scale; however, there is no doubt about the presence of isosbestic points. This implies that the mono- and di-valent diamine cations are in equilibrium. Since these two species are in different oxidation states, if follows that the diamine itself is also a participant in the equilibrium. However, the absence of the absorption to be assigned to the diamine, *i. e.*, 30.0 kK for benzidine and 28.7 kK for tetramethylbenzidine in the solid state, suggests that the diamine molecules in acid clay are in the protonated form.

Summing up our conclusions, the following equilibrium may be conceived in acid clay:

$$D^{2+} + DH^{+} \rightleftharpoons 2D^{+} + H^{+},$$

where D is a diamine molecule. On being moistened, protonated diamine molecules dissociate into protons and diamine molecules, and the electron transfer from the latter to the divalent cations leads to the formation of deeply-colored aggregates of the monovalent cations. According to the proposed mechanism of the lightening of the color on drying and the deepening on moistening, Hauser and Leggett have observed that mineral and organic acids either inhibit or lighten the color.[2] Moreover, the same equilibrium as that described above has been proposed by Hasegawa to explain the pH dependence of the absorption spectrum of the "meriquinoid compound" of tetramethylbenzidine in a 30% ethanol solution.[3]

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[8] H. Matsusaka and K. Suzuki, Paper presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.