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The Diffuse Reflection Spectra of Bentonites Colored with Various Aromatic Compounds and Related Ion-radical Salts

Yoshio MATSUNAGA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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Bentonites colored with each of the following aromatic compounds were examined by the method of diffuse reflection in the range from 4 to 30 kK: benzidine, 4,4′-dihydroxybiphenyl, 4,4′-dimethoxybiphenyl, perylene, tetrathiotetracene, and phenothiazine. By comparison with the spectra of the related ion-radical salts, the oxidation of the aromatic compounds to the mono- and/or di-valent cations could be proven in all of them. Except in the case of phenothiazine, the species in the colored clays was found to be drastically modified by moisture. In addition, the spectra of the copper-arene complexes recently reported by Mortland *et al.* were measured. The oxidation of perylene, tetrathiotetracene, and phenothiazine was found to proceed to a greater extent in the copper-exchanged clays.

Earlier we examined the coloration of acid clay upon the addition of benzidine and related aromatic diamines and showed that the diamines are oxidized to the mono- and di-valent cations.[1] The former cations were found to be in various modes of intermolecular interaction, depending on the kind and amount of the liquid. For instance, acid clay colored with benzidine is blue when moistened with water and yellow when dried. The spectrum of the wet sample consists of bands at 7.5, 12.0, 17.0, and about 27 kK, and closely resembles that of the solid benzidine bromide, where the monovalent diamine cations are supposed to be in a strong, more-than-by-pairs interaction.[2] The spectrum displayed by the dried sample has only one absorption maximum, located at 22.5 kK. Between these two situations, a pattern with maxima at 9.5, 14.5, and 26 kK and a shoulder at 16 kK can be observed by carefully controlling the amount of water. This spectrum can be more easily developed by moistening with methanol instead of water. Finally, when benzene is added to the dried sample, absorption maxima appear at 11.5, at 15.2, and somewhere around 27 kK. The last is similar to that of the dimeric cation in solution and is assigned to the cations in a pair-by-pair interaction.

Bentonite, a clay of the montmorillonite type, has been well known to be colored with aromatic amines;[3–5] therefore, it seemed interesting to study the spectra of bentonites colored with benzidine and to compare them with those of the colored acid clay. In recent years, the formation and stabilization of the monovalent cation from aromatic compounds by contact with silica-alumina and synthetic zeolite has been extensively examined by several workers.[6–10] On the other hand, a limited amount of work has been done on the coloration of natural clays with aromatic compounds other than amine. Takahashi observed that acid clay turns green upon the addition of 4,4′-dihydroxybiphenyl dissolved in aqueous ethanol.[5] Recently Mortland *et al.* reported that the color of well-dried copper(II) bentonite changes from a pale blue to dark red when exposed to benzene vapor.[11,12] Similarly, toluene forms a bright green complex, and xylene, a dark purple complex. In the present work, the following were selected in order to cover various types of aromatic compounds: benzidine, 4,4′-dihydroxybiphenyl, 4,4′-dimethoxybiphenyl, perylene, tetrathiotetracene, and phenothiazine. The ion-radical salts derived from most of these compounds are available, so that the spectra of the colored bentonites can be compared with those of the oxidized forms. The cupric ion has been found necessary to the coloration with benzene; the effect of the cation exchange was examined with perylene, tetrathiotetracene, and phenothiazine.

Experimental

Materials. Natural bentonite supplied by the Koso Chemical Co., Ltd., was refined by repeated elutriations. The colored clays were prepared by grinding an organic compound and the clay together in a ratio of 1 : 99 by weight. If the color was not well developed by this technique, a small amount of chloroform was added to the mixture. The copper exchange was carried out following the procedure given by Yariv *et al.*[13] As this clay was found not to be intensely colored with benzene, the copper-exchanged clay prepared from Wyoming bentonite was mostly employed in the rest of the work.

Van Alphen's 4,4′-dimethoxybiphenyl dinitrate was obtained by the addition of a mixture of fuming nitric acid and carbon tetrachloride to the compound dissolved in carbon tetrachloride.[14] The sodium salt of *p*-diphenosemiquinone was made by the oxidation of 4,4′-dihydroxybiphenyl dissolved in aqueous sodium hydroxide with ferricyanide ions, as has been described by Willstätter and Kalb.[15] The solid

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[1] A. Hakusui, Y. Matsunaga, and K. Umehara, This Bulletin, **43**, 709 (1970).

[2] Y. Iida and Y. Matsunaga, *ibid.*, **41**, 2615 (1968).

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

[4] H. Weil-Malherbe and J. Weiss, *J. Chem. Soc.*, **1948**, 2164.

[5] H. Takahashi, This Bulletin, **28**, 5 (1955).

[6] N. Okuda and T. Tachibana, *ibid.*, **33**, 863 (1960).

[7] J. J. Rooney and R. C. Pink, *Trans. Faraday Soc.*, **58**, 1632 (1962).

[8] W. K. Hall, *J. Catal.*, **1**, 53 (1962).

[9] D. M. Brouwer, *ibid.*, **1**, 372 (1962).

[10] D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, **86**, 749 (1964).

[11] H. E. Donor and M. M. Mortland, *Science*, **166**, 1406 (1969).

[12] M. M. Mortland and T. J. Pinnavaia, *Nature Phys. Sci.*, **229**, 75 (1971).

[13] S. Yariv, L. Heller, Z. Sofer, and W. Bodenheimer, *Israel J. Chem.*, **6**, 741 (1968).

[14] J. van Alphen, *Rec. Trav. Chim.*, **49**, 767 (1930).

[15] R. Willstätter and L. Kalb, *Ber.*, **38**, 1232 (1905).

salts of the mono- and di-valent tetrathiotetracene cations were prepared according to the methods of Marschalk and Niederhauser.[16)]

Measurements. The spectra were recorded on a Beckman DK 2A spectrophotometer with the aid of a reflectance attachment.[1)] The colored clays were moistened by leaving them in a desiccator containing water, while they were dried in a desiccator containing silica gel. If stable, the clays were dried in an oven kept near 100°C.

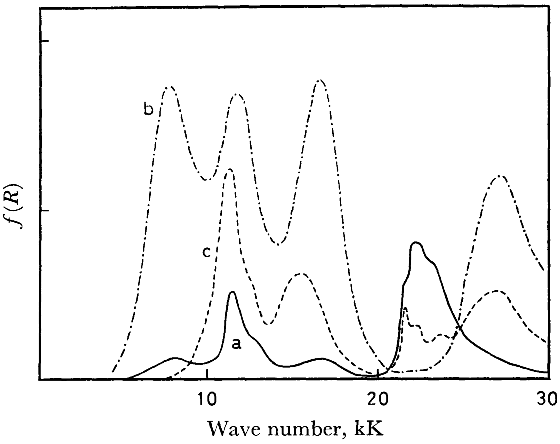

Fig. 1. Diffuse reflection spectra of benzidine-bentonite; (a) prepared by grinding, (b) moistened with water, (c) moistened with benzene.

Results and Discussion

Benzidine-bentonite (Fig. 1). When benzidine and the clay are ground together, absorption bands appear at 11.5, about 13, 21.6, 22.2, and about 23 kK. This spectrum, Curve a in Fig. 1, is in good agreement with that of the monovalent benzidine cation in an ethanolic solution at room temperature. The latter is known to have bands at 11.6 and 13.3, a shoulder at 14.3, and a strong band with a vibrational structure around 22 kK. Therefore, the cation formed at this stage is essentially free from intermolecular interaction. Upon moistening with water, a pattern with bands 7.8, 11.7, 16.6, and 27.3 kK is developed (see Curve b). The locations are close to those in the B-1 pattern which is observed in the wet benzidine-acid clay, as was reported in our earlier paper. The same pattern can be seen as the background of Curve a. However, the band at 7.8 kK becomes relatively less intense when the sample is partially dried. This observation leads to the conclusion that the spectrum given by Curve b is a superposition of the spectra of two species. The sample moistened with benzene exhibits bands at 11.3, 15.5, and 27.0 kK and a shoulder around 12.4 kK. This pattern can well be compared with the B-3 pattern recorded with the colored acid clay moistened with the same solvent. As this spectrum is similar to that of the dimeric form of the benzidine cation observed in a cold ethanolic solution,[17)] the monovalent cations here may be supposed to be essentially in a pair-by-pair interaction. The spectrum shown by Curve b may be explained as a superposition of the B-1 and B-3 patterns. As was mentioned in our previous paper, the cations exhibiting the former pattern are likely in a more-than-by-pairs interaction, and this fraction is apparently increased by the presence of water. The band with some structure appearing in the range from 21 to 24 kK of Curve c indicates that the monomeric cations are left in this sample. Because of the presence of isosbestic points at 20.7 and 24.7 kK among the a, b, and c Curves, it may be concluded that the species giving the spectra shown by Curves b and c are in equilibrium with the monomeric cations.

Although a broad background, possibly arising from some decomposition products, appears upon drying, the pattern of the monomeric action reappears. It must be noted that this behavior is quite different from that found in the benzidine-acid clay. In the latter case, the dried sample is yellow and its spectrum has only one absorption maximum, at 22.5 kK which has been assigned to the divalent cation, the quinoidal form in Hasegawa's nomenclature.[1),18)] This species is consumed in the development of the blue color in the acid clay upon moistening. From these observations, it can be argued that the mean oxidation state of benzidine in the bentonite complex is lower than that in the acid clay complex.

Dihydroxybiphenyl- and Dimethoxybiphenyl-bentonites (Figs. 2 and 3). 4,4′-Dihydroxybiphenyl, which has an isoelectronic structure with benzidine, gives a green-colored complex with bentonite.[5)] A relatively weak band at 14.0 kK and a strong one at 24.2 kK are generated in the moistened sample. Both of them disappear when dried. The behavior of the dimethoxybiphenyl complex is essentially the same as has been described above (compare Curves a and b in Fig. 2). No cation-radical salt derived from dihydroxybiphenyl is known; however, salts of the $OC_6H_5 \cdot C_6H_5O^-$ anion, which is isoelectronic with the $HOC_6H_5 \cdot C_6H_5OH^+$ cation, are available. Figure 3 presents the spectrum of the solid sodium salt as well as the spectrum in an

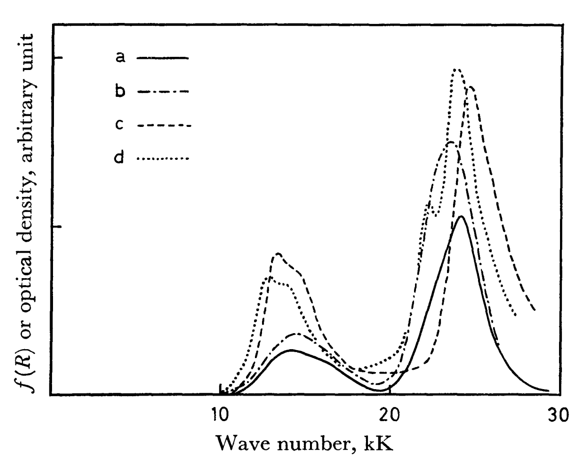

Fig. 2. Diffuse reflection spectra; (a) dihydroxybiphenyl-bentonite, (b) dimethoxybiphenyl-bentonite and absorption spectra of sulfuric acid solutions; (c) dihydroxybiphenyl, (d) dimethoxybiphenyl.

[16)] C. Marschalk and J. P. Niederhauser, *Bull. Soc. Chem. France*, **1952**, 151.

[17)] K. Takemoto, H. Matsusaka, S. Nakayama, K. Suzuki, and Y. Ooshika, This Bulletin, **41**, 764 (1968).

[18)] H. Hasegawa, *J. Phys. Chem.*, **65**, 292 (1961).

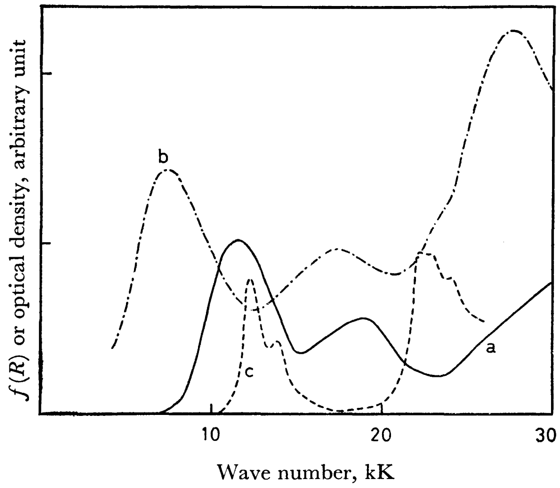

Fig. 3. Diffuse reflection spectra; (a) sodium salt of *p*-diphenosemiquinone, (b) van Alphen's dimethoxybiphenyl dinitrate and absorption spectrum of *p*-diphenosemiquinone ion in ethanol (c).

ethanolic solution. The former exhibits absorption maxima at 11.5 and 19.0 kK, and the latter, at 12.2, at 13.8, and around 22 kK. As to dimethoxybiphenyl, the blue-colored dinitrate prepared by van Alphen has been reported by Buck *et al.* to show an ESR absorption.[19] This observation may be considered as an indication that the salt contains a monovalent cation rather than a divalent one; therefore, we will examine the spectrum of this dinitrate (see Curve c of Fig. 3).

As this compound is not stable, especially when diluted for the spectral measurements, the recorded spectrum is distorted because of the fading during the measurement. A comparison with the spectrum recorded without dilution suggests that the band at 7.4 kK is as intense as that at 27.5 kK. Among the spectra presented in Fig. 3, only the spectrum of *p*-diphenosemiquinone ion dissolved in ethanol bears some resemblance to those of the colored clays. However, the intensity ratio of the low-energy band to the high-energy one in the monovalent anion is far larger than that observed with the colored clay. In addition, the former spectrum is shifted to the low-energy side as much as several kK compared to the latter.

Hydroquinone and 1,4-dimethoxybenzene, closely related to the present compounds, have been known to be converted into monovalent cations upon being dissolved in concentrated sulfuric acid.[20] Therefore, the measurements of the spectra of dihydroxybiphenyl and dimethoxybiphenyl in sulfuric acid were attempted. The spectra recorded immediately after the dissolution are similar to each other, as is shown in Fig. 2. These species are transitory. In the case of dimethoxybiphenyl, the band at 22.2 kK is considerably increased on standing. As we may expect on the basis of their isoelectronic structures, the spectrum of the dihydroxybiphenyl cation is similar to that of the monovalent anion given in Fig. 3. Nevertheless, the general shift to the high-energy side and the enhancement of the high-energy band make the spectrum closer to that of the bentonite complex. Thus, it is very likely that the species in the colored clays are the monovalent cations derived from these compounds.

It should be noted that, although the spectrum of the *p*-diphenosemiquinone ion in ethanol is essentially the same as those of the tetrahalo derivatives reported earlier, the solid-state spectrum is markedly different from those of the derivatives. For example, the sodium salt of 3,3′,5,5′-tetrachloro-*p*-diphenosemiquinone shows a solid-state spectrum composed of three bands located at 6.8, 15.5, and 26.4 kK.[21] This feature is rather similar to that of the spectrum of the dimethoxybiphenyl dinitrate, which consists of bands at 7.4, 17.4, and 27.5 kK. In accordance with the results of the ESR measurement made by Buck *et al.*, this spectral similarity and the presence of an absorption maximum as low as 7.4 kK strongly suggest that the cation in the dinitrate is monovalent rather than divalent, and that it is in a more-than-by-pairs interaction. The tetra-*n*-propylammonium salt of tetrabromo-*p*-diphenosemiquinone has been found to show a spectrum consisting of bands located at 11.5, 15.2, and 24.5 kK. Because these locations nearly correspond to those in the dimeric form of the benzidine cation (12.4, 16.4, and 28 kK), the monovalent anions in this ammonium salt have been assumed to be in a pair-by-pair interaction.[21] Although the location of the middle band in the spectrum of the sodium salt of unsubstituted *p*-diphenosemiquinone does not agree with the corresponding band in the above-mentioned ammonium salt, the semiquinone ions here might also be in a pair-by-pair interaction.

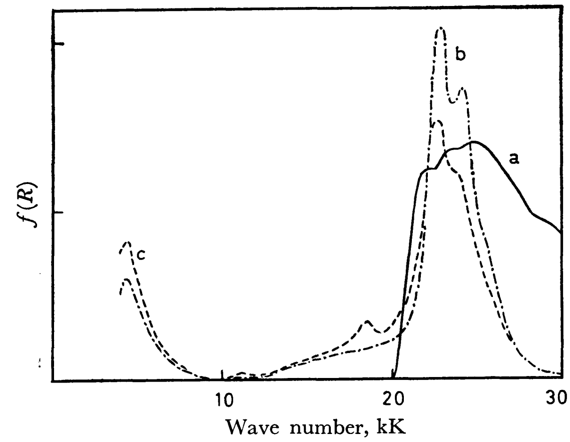

Fig. 4. Diffuse reflection spectra; (a) perylene, (b) perylene-bentontie, dried, (c) the same, moistened.

Perylene-bentonite (Fig. 4). The dried sample is yellow, but it is darker than the hydrocarbon itself because of the presence of a tail extending into the near-infrared region. In addition, the presence of a band at 4.4 kK must be noted. Upon moistening, this low-energy band is intensified and the bands corresponding to those of perylene are weakened (compare Curves b and c in Fig. 4). Furthermore, the appearance of a little peak is observed at 18.5 kK, where the well-known

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19) H. M. Buck, J. H. Lupinski, and L. J. Oosterhoff, *Mol. Phys.*, **1**, 196 (1958).

20) K. Kimura and H. Yamada, This Bulletin, **42**, 3032 (1969).

21) Y. Matsunaga and Y. Narita, *ibid.*, **45**, 408 (1972).

monovalent cation exhibits a strong sharp absorption.[22-24] The weak absorptions in the range from 12 to 20 kK may be considered as a part of the spectrum of the perylene cation. In the solid-state spectrum of perylene perchlorate reported by Sato *et al.*, the low-energy band is found at 7.7 kK;[25] it arises from the interaction between the cations. On the other hand, the band appearing at 4.4 kK in the colored clay may be attributed to the interaction between the cation and the neutral molecule. Very recently Chiang *et al.* reported the preparation of (perylene)$_2$ ClO$_4$,[26] where such an interaction may be expected to be observed. Unfortunately, though, no spectrum was given for this ion-radical salt.

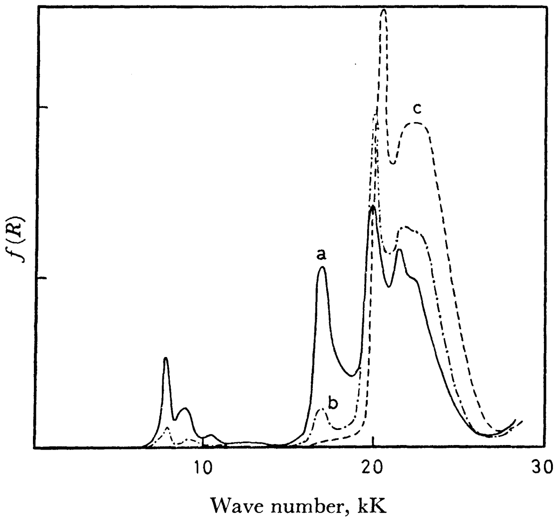

Fig. 5. Diffuse reflection spectra; (a) tetrathiotetracene-bentonite, dried, (b) the same, moistened, (c) tetrathiotetracene-Cu bentonite, dried.

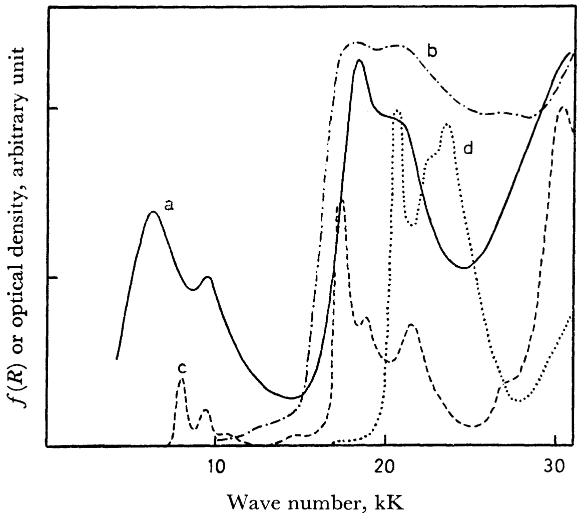

Fig. 6. Diffuse reflection spectra; (a) (tetrathiotetracene$^+$)$_2$SO$_4$, (b) tetrathiotetracene^{++} (HSO$_4$)$_2$ and absorption spectra; (c) the monovalent cation in ethanol, (d) the divalent cation in dilute acid.

Tetrathiotetracene-bentonite (Figs. 5 and 6). When a mixture of tetrathiotetracene and clay is moistened with chloroform, it turns dark red and then yellow. The red color reappears easily when it is dried in an oven. This color change is reproducible and can be observed even after storage for over a year. As may be seen by a comparison of Curves a and b in Fig. 5, the spectrum is a superposition of two patterns. One of them consists of three weak bands in the range from 7 to 11 kK and two strong ones located at 17.0 and 21.4 kK. The other has a sharp band at 20 kK and a rather broad one around 22 kK. As will be mentioned in the next paragraph, the former pattern can be ascribed to the monovalent cation, and the latter, to the divalent cation. Both of them seem to be free from intermolecular interactions. The equilibrium between these two species moves to the divalent cation upon the addition of moisture, as is shown in Fig. 5. In addition, the measurements of the spectrum in the range from 100 to 150°C, which is selected to avoid the effect of moisture, revealed the movement of the equilibrium towards the monovalent cation upon an elevation of the temperature.

Since the preparation of dark green-colored tetrathiotetracene, it has been discovered to be easily oxidized to the red-colored monovalent cation and the yellow-colored divalent cation. Several pairs of the salts of these two cations have been isolated by Marschalk and Niederhauser.[16] Moreover, tetrathiotetracene forms ionic molecular complexes with many strong electron-acceptors.[27] The spectra of the solid monobromide and the *o*-chloranil complex have been measured, and their red color has been attributed to bands appearing around 20 kK. To elucidate the species in the colored clays, the spectra of (tetrathiotetracene$^+$)$_2$SO$_4$ and tetrathiotetracene^{2+}(HSO$_4$)$_2$ were examined in both the solid and dissolved states. The former salt exhibits absorption maxima at 6.3, 9.5, and 18.4 and a shoulder at 21 kK. On the other hand, the spectrum of the monovalent cation in ethanol is characterized by the presence of three weak maxima, at 8.0, 9.5, and 10.7 kK, and a strong maximum at 17.3 kK. It must be noted that the bands in the near-infrared region are very much more widened and intensified in the solid state than in the dissolved state. The spectrum of the brown-colored bisulfate is rather similar to the above-mentioned in the visible region; that is, the maxima are found at 18.0 and 20.8 kK. However, no absorption is detected in the infrared region. When dissolved in dilute acid, the absorption bands become sharper and are shifted to 20.7 and 23.6 kK respectively. Furthermore, a shoulder at 22.7 kK can be observed (see Curve d in Fig. 6). Apparently the spectra of the colored clays are close to those of the cations in the dissolved state. We also examined the solid-state spectra of tetrathiotetracene$^+$ Cl·H$_2$O, tetrathiotetracene$^+$ Br, and tetrathiotetracene$^+$ NO$_3$. They are similar to the above-mentioned spectrum; however, the intensity ratio

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[22] G. J. Hoijtink and W. P. Weijland, *Rec. Trav. Chim.*, **76**, 836 (1957).

[23] W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049.

[24] H. Kuroda, T. Sakurai, and H. Akamatu, This Bulletin, **39**, 1893 (1966).

[25] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *ibid.*, **42**, 3051 (1969).

[26] T. C. Chiang, A. H. Reddoch, and D. T. Williams, *J. Chem. Phys.*, **54**, 2051 (1971).

[27] Y. Matsunaga, *ibid.*, **42**, 2248 (1965).

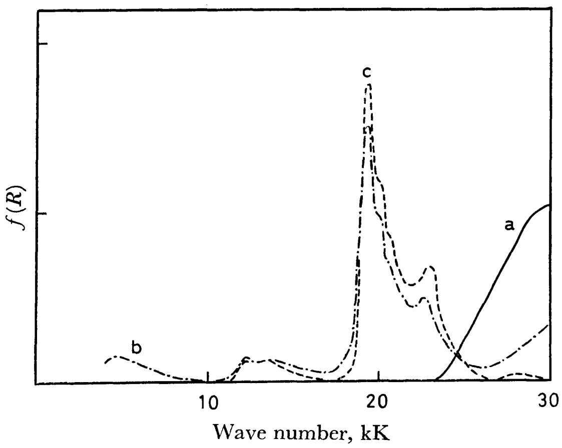

Fig. 7. Diffuse reflection spectra; (a) phenothiazine, (b) phenothiazine-bentonite, (c) phenothiazine-Cu bentonite.

between the band in the infrared region and that in the visible region depends markedly on the kind of anion; that is, it is 0.76: 1 in the chloride, 0.65: 1 in the bromide, 0.60: 1 in the sulfate, and 0.20: 1 in the nitrate.

Phenothiazine-bentonite (Fig. 7). The spectrum of this colored clay in the region between 10 and 25 kK is in good agreement with that of the monovalent cation in solution.[28] However, there are extra absorptions — a weak one in the infrared region and a relatively strong one above 25 kK (see Curve b in Fig. 7). The former may be due to the interaction between the cation and the neutral molecule, for the latter agrees well with that of phenothiazine itself. As was reported earlier, the solid semiquinoid bromide may show an absorption in the infrared region.[29] Nevertheless, the possibility that the weak absorption with a maximum at 4.7 kK in the colored clay is due to the interaction between the cations may be ruled out, because the spectrum of the colored clay between 10 and 25 kK is far from the solid-state spectrum of the bromide. No clear effect of moisture is noted in this case.

Mortland's Copper-arene Complexes (Fig. 8). It has been reported by Donor and Mortland that the benzene complex of copper(II)-exchanged Wyoming bentonite is green or gray when partially hydrated and dark red when well dried.[11] On the basis of the vibrational spectra, Mortland and Pinnavaia have concluded that the green form of coordinated benzene possesses a D_{6h} local symmetry, while the red form does not.[12] It has been suggested that a reduction in the symmetry of the benzene ring occurs if the copper(II) ion is bonded to an edge of the ring, as in the copper(I) complex C_6H_6-$CuAlCl_4$. As no electronic spectrum has been reported by them except for the statement that a very broad intense absorption extends from 1.7 to beyond 4.0 kK, the diffuse reflection spectra of these two forms of the benzene complex as well as those of the toluene and *p*-xylene complexes were measured.

The spectrum of the red form of the benzene complex has a broad maximum located at 19.4 kK and a shoulder around 23 kK in the visible region, and a very intense maximum at 4.4 kK. The electronic absorption mentioned by Mortland and Pinnavaia must be the tail of the last-named one. When this sample is exposed to ambient temperatures and humidity for a while, it turns gray. Contrary to the remarkable change in the vibrational spectrum reported by Mortland, the only change found in the electronic spectrum is the appearance of an additional strong band at 26.7 kK. The low-energy band of the green toluene complex is located at about 10 kK, and that of the purple *p*-xylene complex, at about 9 kK. Compared to the low-energy band of the benzene complex, they are appreciably weaker and at higher energies.

Perylene-Cu Bentonite (Fig. 9). After drying in an oven, the color is a bluish violet. The spectrum between 10 and 20 kK is essentially that of the monovalent cation (see Curve a). Nevertheless, the band in the infrared region and the one at 22.6 kK cannot be assigned to this ion. Upon moistening, the absorptions due to the cation become less intense, while the other two become more intense. The latter pattern is different from both the spectrum of the dimeric perylene cation, which has been shown by Kimura *et al.* to have bands at 10 and 20 kK,[30] and the spectrum of the

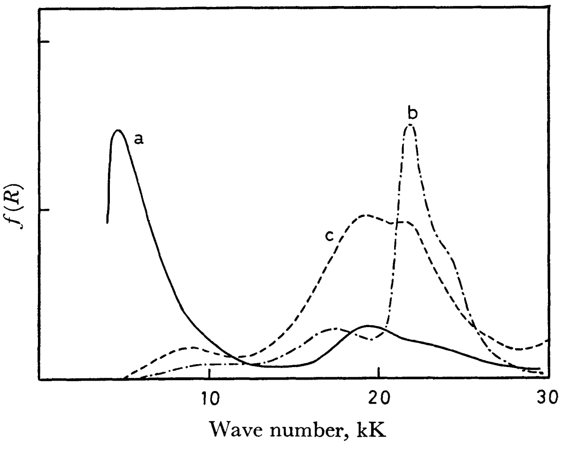

Fig. 8. Diffuse reflection spectra of Mortland's copper-arene complexes; (a) the benzene complex, (b) the toluene complex, (c) the *p*-xylene complex.

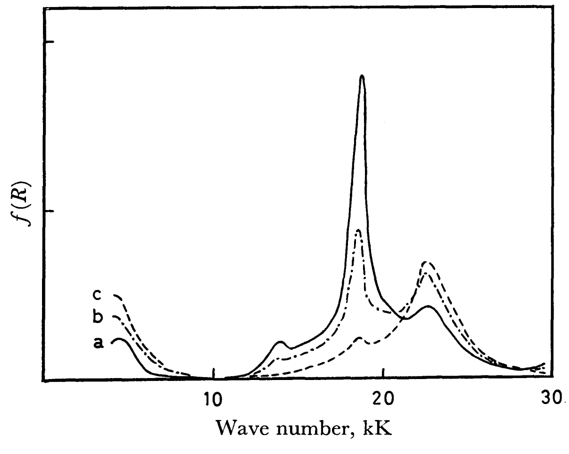

Fig. 9. Diffuse reflection spectra of perylene-Cu bentonite; (a) dried, (b) moistened, (c) moistened further.

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[28] H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1965).

[29] Y. Matsunaga and K. Shono, This Bulletin, **43**, 2007 (1970).

[30] K. Kimura, T. Yamazaki, and S. Katsumata, *J. Phys. Chem.*, **75**, 1768 (1971).

solid cation-radical salt studied by Sato *et al.*[25] Therefore, the species to which the new pattern is assignable may be the divalent cation or the neutral molecule. The electronic spectra of the alternant hydrocarbon cation and anion of the same valency may theoretically be expected to be practically identical.[31] As the spectrum of the divalent anion of perylene reported by Balk *et al.* bears no resemblance to the above-mentioned pattern,[32] it is not likely that a hitherto-unknown divalent cation is the major species in the moistened sample. The absorption at 22.6 kK may be attributed to the neutral molecule, and that in the infrared region, to the interaction between the monovalent cation and the neutral molecule. If this interpretation is correct, the effect of moisture on the equilibrium is in the direction opposite to that observed with the perylene-unexchanged bentonite. Finally, it must be added that the coexistence of perylene and its monovalent cation has been noted in experiments on the oxidation of this hydrocarbon by silica-alumina.[8,9]

Tetrathiotetracene-Cu Bentonite. The only species found in this sample is the yellow-colored divalent cation (see Curve c in Fig. 5).

Phenothiazine-Cu Bentonite. The spectrum is presented in Fig. 7 (see Curve c). There are no absorptions but those arising from the monovalent cation. Contrary to the case of phenothiazine-bentonite, the oxidation appears to be complete. The same tendency has already been noted in the other two cases discussed above.

As the species in the colored bentonites are mono- and/or di-valent cations, one may expect that the ionization potentials of these aromatic compounds correlate with the degree of the oxidation by bentonite, as has been demonstrated with silica-alumina.[33] The energy of the charge-transfer absorption generated by mixing with *p*-chloranil in chloroform is 1.52 eV for phenothiazine, 1.64 eV for perylene, 1.81 eV for benzidine, and 2.20 eV for dimethoxybiphenyl.[34] The ability to donate an electron should decrease in this order. The solid-state ionization potentials of perylene and tetrathiotetracene have been estimated to be 5.33 and 4.42 eV respectively by the photoemission method.[35] Thus, tetrathiotetracene is the best electron-donor among the compounds examined and, in fact, is the only compound to form the divalent cation when added to bentonite. The presence of the neutral molecule is noted in the cases of phenothiazine and perylene. In accordance with the order of the ionization potential, the latter spectrum is more dominated by the unionized component than is the former. The coloration of bentonite with the poorest donors, dihydroxybiphenyl and dimethoxybiphenyl, is very faint. Possibly only a small part of the added compound is oxidized to the monovalent cation. However, benzidine does not seem to show the tendency observed above. The absorption to be assigned to benzidine, 30.0 kK in the solid state, is absent in Fig. 1. This anomaly may be due to the protonation. If so, the absorption is not in the range covered by the present work. It should be pointed out that all the monovalent cations except the benzidine cation are found to be essentially free from mutual interaction. Apparently this observation cannot be explained by the difference in the concentration of the monovalent cation.

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31) W. P. Weijland, Thesis, Free University, Amsterdam (1958), cited in Ref. 23.

32) P. Balk, G. J. Hoijtink, and J. W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 813 (1957).

33) G. M. Muha, *J. Phys. Chem.*, **74**, 2939 (1970).

34) G. Saito and Y. Matsunaga, This Bulletin, **44**, 1788 (1971).

35) M. Kochi, Y. Harada, T. Hirooka, and H. Inokuchi, *ibid.*, **43**, 2690 (1970).