

REACTIVITY OF ADSORBED AND STRUCTURAL IRON IN HECTORITE AS INDICATED BY OXIDATION OF BENZIDINE

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Abstract—The roles of different forms of Fe(III) impurities in a hectorite with respect to the oxidation of benzidine in aqueous suspension have been evaluated using electron spin resonance and UV-visible spectroscopy. Natural surface-adsorbed Fe(III) showed no detectable activity in the oxidation process, while very small quantities of structural octahedral Fe(III) apparently promoted a relatively rapid conversion to the radical cation. However, extremely small quantities of benzidine were oxidized in comparison to the exchange capacity of the clay. Freshly adsorbed Fe^{3+} cations effectively oxidized benzidine, but lost much of this ability upon aging. The Fe(III)-benzidine electron transfer could be distinguished from an O_2 -benzidine reaction, since the latter reaction was slow and limited by the rate of O_2 diffusion into the clay-water system. The O_2 -benzidine reaction was also inhibited at high pH. The existence of two reaction mechanisms and the involvement of only a small fraction of the total structural iron, as shown by comparison of the hectorite and a montmorillonite, may explain the conflicting interpretations in the literature. The benzidine blue reaction not only requires an oxidizing agent to form the radical, but also a clay surface to adsorb and stabilize it against further oxidation.

Key Words—Adsorbed Iron, Benzidine, Catalysis, Electron Transfer, Hectorite, Oxidation.

INTRODUCTION

The ability of clay minerals to catalyze certain oxidation reactions of organic molecules is well known. For example, many montmorillonites promote the conversion of benzidine to the blue monovalent semiquinone (Theng, 1974), hydroquinone to p-benzoquinone (Thompson and Moll, 1973), and pyrogallol to quinones of poorly defined structure (Kumada and Kato, 1970). However, the mechanisms of catalysis have been the subject of considerable speculation. It is generally agreed that structural Fe^{3+} is at least partly responsible for the oxidation reactions, but Al^{3+} substituted for Si^{4+} in tetrahedral sites (Dodd, 1955) as well as Al^{3+} at edge sites (Solomon *et al.*, 1968) have been suggested as active sites in the oxidation of organics on clays containing little or no iron. The lack of basic understanding of the surface reactions has greatly limited the utility of these reactions for the classification of clays and other purposes. A more detailed and quantitative approach, utilizing spectroscopic techniques such as UV-visible and electron spin resonance (ESR), may determine those factors which affect the surface reactions, and resolve a number of inconsistencies in the literature. The present investigation examines the role of ferric iron in the clay-catalyzed oxidation of benzidine.

MATERIALS AND METHODS

Natural hectorite obtained from the Baroid Division of NL Industries with a cation-exchange capacity (CEC) of 71 meq/100 g, was used for most of the experiments. Free iron oxides were removed from a portion of the clay by the standard citrate-dithionite extraction procedure in order to evaluate the influence of

nonstructural Fe impurities on the ability to oxidize benzidine. The Ca^{2+} -saturated form of Upton, Wyoming, montmorillonite (CEC = 92 meq/100 g) was used in selected experiments as a comparison with hectorite, since it contained a much greater amount of structural Fe^{3+} .

ESR spectra of the minerals before and after reaction with aqueous benzidine solutions were obtained on a Varian E-104 (X-band) spectrometer, often with oriented clay films aligned perpendicular (\perp) or parallel (\parallel) to the magnetic field of the spectrometer. Equilibrations between clay films and benzidine which required the exclusion of O_2 were done by continuous bubbling of N_2 through the system. The UV-visible spectra of dispersed aqueous suspensions of clay-benzidine complexes were recorded on a Perkin-Elmer Model 200 spectrophotometer with integrating sphere attachment. A number of equilibrations were conducted with 100-mg or 10-mg samples of these clays in 4.1×10^{-5} and 4.1×10^{-4} M aqueous benzidine solutions. The quantity of benzidine adsorbed was measured by the decrease in the intensity of the UV absorbance of the supernatant at 283 nm after centrifuging to separate the clay.

RESULTS AND DISCUSSION

Form of Fe^{3+} in hectorite

Hectorite is known to produce a faint blue color when combined with benzidine, and surface-adsorbed contaminants or structural Fe^{3+} have been suggested as the source of this reactivity (Solomon *et al.*, 1968). The ESR spectra of Figure 1 show that both of these components are present in hectorite. The ESR signal at $g =$

4.3 is indicative of octahedral Fe^{3+} in the clay, while the very broad signal closer to $g = 2$ can probably be attributed to ferromagnetic, surface-adsorbed iron oxides or hydroxides (Angel and Vincent, 1978) since it is greatly reduced by a single citrate-dithionite treatment (Figure 1B). It was also noted that the citrate-dithionite treatment resulted in the appearance of a Mn^{2+} signal from the clay, suggesting that Mn oxides were also present in the hectorite.

The anisotropy of the $g = 4.3$ signal is clearly shown in Figure 1C. It is very similar to the orientation-dependence of the Fe^{3+} signal in Upton montmorillonite (Berkheiser and Mortland, 1975) but is in the *opposite* sense. The higher field shoulder appears for the \perp rather than \parallel orientation of the hectorite film relative to the magnetic field. This difference may be due to the fact that hectorite is a trioctahedral mineral while montmorillonite is dioctahedral. Thus, the ligand field of Fe^{3+} would be expected to have different symmetries in the two clays. The very broad signal attributable to surface-adsorbed iron oxides also shows anisotropy, shifting upfield when the clay platelets are aligned perpendicular to the magnetic field (Figure 1A). This implies some degree of order of the oxide impurities relative to the clay surface which can qualitatively be explained by electron spin-spin interaction. Surface-adsorbed hydroxy polymers of Fe^{3+} could result in relatively close Fe-Fe distances in the plane of the clay platelets. For alignment of the magnetic field \perp and \parallel to the clay films, a line joining neighboring Fe atoms would describe a 90° and 0° angle, respectively, to the magnetic field. If this angle is symbolized as θ , and r is defined as Fe-Fe distance, then the local magnetic field at the Fe atom arising from the spin of a neighboring atom is given by (Wertz and Bolton, 1972):

$$H_{\text{local}} = \mu_e(1 - 3 \cos^2\theta)/r^3$$

where μ_e is the electron dipole moment of the $S = 5/2$ Fe^{3+} ion. Thus, it can be shown that the \perp orientation of the clay film should shift the resonance position upfield because H_{local} subtracts from the applied magnetic field. For the \parallel orientation, H_{local} adds to the magnetic field, thereby shifting the resonance downfield. Therefore, surface-adsorbed iron could account for the spectral shift observed in Figure 1A. This anisotropy was not observed for hectorite that had been treated with Fe^{3+} and washed to allow hydrolysis of the adsorbed iron, although a broad resonance centered near $g = 2$ was produced by this treatment. The results suggest that natural adsorbed iron is more ordered at surfaces than that added by salt treatment.

The possible effect of the naturally adsorbed iron on the exchange properties of the hectorite was checked by determining CEC values before and after iron removal by citrate-dithionite treatment. The CEC values, as measured by MgSO_4 conductometric titration of

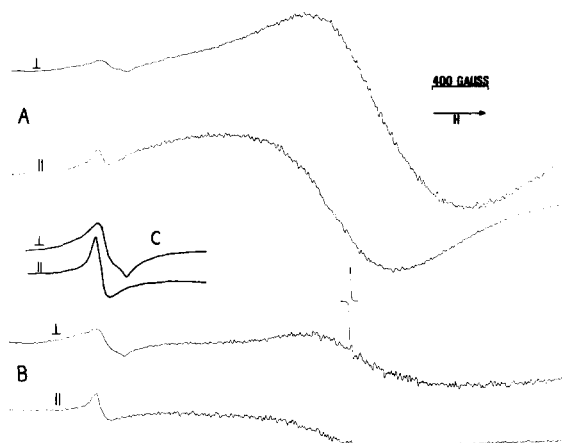


Figure 1. The ESR spectra of air-dried hectorite films; A, untreated; B, citrate-bicarbonate-dithionite treated. The films were oriented \perp and \parallel to the magnetic field. The $g = 4.3$ signal is shown at higher gain in spectrum C. (The free electron position, $g = 2.0023$, is indicated by the narrow resonance near center field.)

Ba^{2+} -saturated clay, were 71 and 75 meq/100 g for the untreated and citrate-dithionite treated hectorite, respectively. Thus, the adsorbed iron did not occupy many exchange sites of the clay.

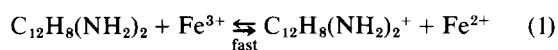
Additional ESR studies of different particle-size fractions of the untreated hectorite, using centrifugation to separate fractions, showed that the $g = 4.3$ signal was *relatively* more intense in the smaller particles, and the anisotropic broad resonance near $g = 2$ became more intense and more isotropic (i.e., orientation-independent) in the larger particles. The trend toward isotropy can be attributed to separate phase, iron oxide impurities that are visible in the coarser fraction. This form of iron should not produce an ESR signal that varies with the orientation of the clay films. Three forms of iron can therefore be identified in the untreated hectorite: structural Fe^{3+} in octahedral sites of the hectorite, surface-adsorbed iron oxides or hydroxides, and separate iron oxide impurities. All must be considered as potential oxidizing agents for the slight conversion of benzidine to benzidine-blue in hectorite.

Mechanism of benzidine-blue reaction on the clay

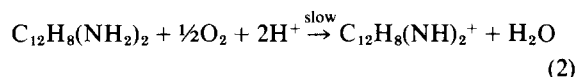
Little difference in the extent of blue color formation within the first few minutes was noted for Mg^{2+} -saturated natural or citrate-dithionite treated hectorite when the clay was soaked in saturated aqueous solutions of benzidine. This indicates that the surface-adsorbed iron is inactive in the rapid oxidation of benzidine. Although freshly precipitated ferric hydroxide also produced no reaction, freshly prepared Fe^{3+} -hectorite showed a very dark blue color after a few minutes of reaction with benzidine. It was also found that Cu^{2+} -

hectorite was very effective in oxidizing benzidine. The unique behavior of the clay is shown by the fact that benzidine added to an aqueous FeCl_3 solution produced a green color initially (which is probably benzidine-blue combined with the yellow color of solution iron or the benzidine dication) which was unstable and quickly precipitated as a brown material. The green solution had a free radical signal detectable by ESR, but the formation of the brown product was accompanied by a rapid loss of signal. Thus, the clay appeared to be necessary to stabilize the blue semiquinone product, playing a more specific role than that of a simple oxidizing agent. This has previously been indicated by the fact that H_2O_2 alone could not form benzidine-blue, but H_2O_2 plus hectorite could (Furukawa and Brindley, 1973).

The faint blue color formed initially on hectorite can be attributed to oxidation by structural Fe^{3+} , since the reaction was not prevented in a N_2 atmosphere. However, with exposure to air, the hectorite became much more intensely blue after several days of reaction, while a N_2 atmosphere prevented this reaction. In addition, a continuous flow of air into the system caused an even more intense blue color in the same period of time, indicating that the slower oxidation of benzidine was limited by the rate of diffusion of O_2 into the suspension. A similar slow reaction was observed previously for benzidine added to hectorite (Furukawa and Brindley, 1973), and attributed to irreversible oxidation by dissolved O_2 . The Upton montmorillonite, in contrast, reacted immediately with benzidine to form a strong blue color, even in a nitrogen atmosphere. Two separate mechanisms appear responsible for the benzidine oxidation, a relatively fast reaction involving structural iron:



and a slower reaction directly involving dissolved or surface-adsorbed O_2 :



Studies have shown that sodium polyphosphate (Calgon) in combination with reduction treatment of the montmorillonite, designed to deactivate crystal edges and structural Fe, respectively, is fully able to prevent color formation (Solomon *et al.*, 1968). However, the interpretation of the data based upon acceptance of electrons at Al atoms seems unlikely. It is more probable that the polyphosphate solution, because of its high pH, inhibits the reaction of benzidine with O_2 (reaction 2), while the reduction of Fe^{3+} to Fe^{2+} prevents reaction (1). In fact, after washing Mg^{2+} -hectorite three times with sodium polyphosphate solution, and rinsing five times, the blue color formation was not inhibited.

The presence of sodium polyphosphate in the benzidine, however, did prevent color formation when clay was added. This effect was not unique to polyphosphate, since 0.1 M NaOH also prevented color formation on hectorite, but did not decrease color formation on Upton montmorillonite. The effect of polyphosphate seems to be one of pH only.

Previous studies noted that Na^+ -montmorillonite develops a blue color in benzidine more rapidly than Ca^{2+} -montmorillonite (Solomon *et al.*, 1968). This could be a pH effect, although slower diffusion of benzidine into the tactoid structures of the Ca^{2+} form of clay may be the explanation, since the final quantity of oxidation did not appear to be greatly affected by the exchange cation. The enhancement of the blue color often observed by addition of NaOH to montmorillonite (Furukawa and Brindley, 1973) appears to be unique to clay systems in which the oxidation involves structural Fe^{3+} , suggesting that $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ interconversion in the clay is pH-dependent.

Reduction of structural iron

Attempts to show significant decreases in intensity of the $g = 4.3$ ESR resonance of hectorite and montmorillonite after reaction with benzidine failed, even when an N_2 atmosphere was used. Since reaction (1) should have reduced the quantity of structural Fe^{3+} , it was concluded that the fraction of Fe^{3+} reduced was very small. A quantitative experiment with 100 mg of Ca^{2+} -montmorillonite equilibrated for one day with 100 ml of 4.1×10^{-4} M benzidine solution confirmed this, indicating that no detectable fraction of the total benzidine had been adsorbed despite the intense blue color of the clay. Repeating the same experiment with a 4.1×10^{-5} M benzidine solution showed that about 80% of the organic was adsorbed in less than 40 minutes, and no further significant adsorption occurred over the next 4 days. However, this amounted to only 3.2 meq/100 g of benzidine semiquinone cations adsorbed by the clay, a quantity that could have been oxidized by a small fraction of the structural Fe^{3+} . Similar experiments with 100 mg and 1.0 g quantities of hectorite equilibrated in 100 ml volumes of 4.1×10^{-5} M benzidine produced no detectable change in the solution concentration of benzidine after 1 to 2 days, despite the appearance of a distinct light blue color on the clay. Clearly, the quantity of benzidine oxidized on hectorite is very small, and can be explained by the reduction of a small fraction of the structural Fe^{3+} impurity.

The reduction of structural iron with the formation of the benzidine radical has been demonstrated by Mössbauer spectroscopy at very high adsorption levels of benzidine with greater benzidine concentrations than used in this study (Tennakoon *et al.*, 1974a). At lower levels of adsorption, no significant change in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio could be observed, in agreement with the

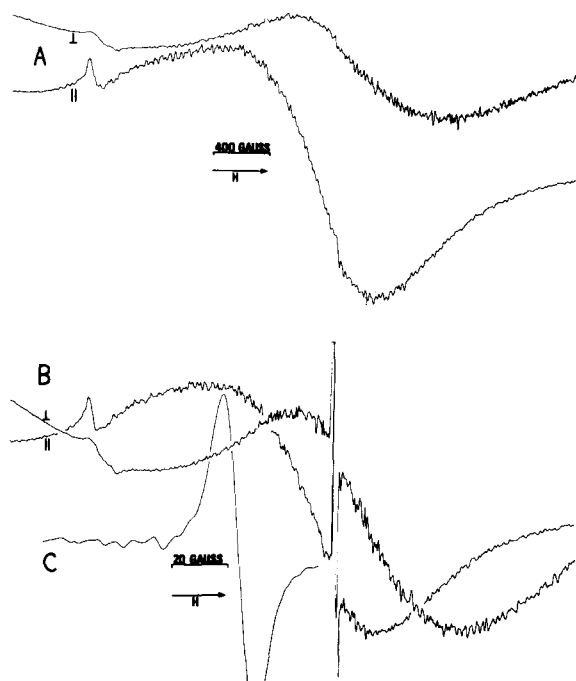


Figure 2. The ESR spectra of untreated Mg^{2+} -hectorite films after 1 day equilibration in a saturated benzidine solution; A, wetted in water (blue form); B, air-dried (yellow form). The free radical signal near $g = 2.00$ that appears in spectrum B is shown in the expanded-scale spectrum (C) for the \perp orientation.

present work. Conceivably, the high level of the adsorbed benzidine radical excludes any source of surface acidity (i.e., exchangeable protons or metal cations), or prevents interlamellar penetration of O_2 molecules by collapse of platelets to a d-spacing of about 15 Å (Tennakoon *et al.*, 1974b). This prevents regeneration of Fe^{2+} to Fe^{3+} by O_2 , and results in a significant decrease of the Fe^{3+}/Fe^{2+} ratio. A direct O_2 reaction with benzidine may be symmetry-forbidden, and O_2 may instead reoxidize the Fe^{2+} produced by the Fe^{3+} -benzidine reaction.

In view of the relatively small fraction of structural iron that actually is involved in the benzidine-blue reaction, probably as a result of structural instabilities created by large quantities of $Fe^{3+} \rightleftharpoons Fe^{2+}$ conversion (Rozenon and Heller-Kallai, 1978), it is not surprising that the reaction seems to be very sensitive to clay pretreatment. For example, heating K^+ -montmorillonite for one hour at $110^\circ C$ produced a 20% increase in the intensity of the $g = 4.3$ ESR signal (an internal ESR standard was used for quantitative accuracy). Such preheating has been shown to enhance the benzidine-blue color reaction (Weil-Malherbe and Weis, 1948). Similarly, the oxidation state of the clay (i.e., Fe^{2+}/Fe^{3+} ratio) is influenced by suspension in water, acidity of the exchange cations, and other factors (Rozenon and

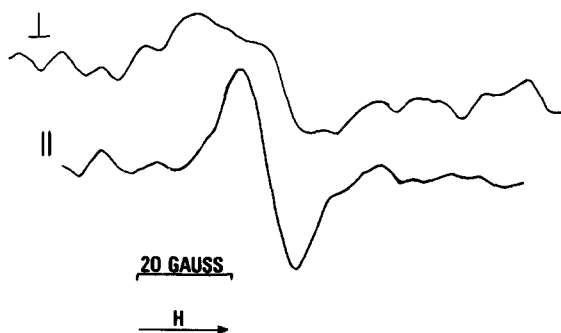


Figure 3. The ESR spectrum of the free radical signal on untreated hectorite films after equilibration in benzidine solution and allowing to air-dry to the yellow form.

Heller-Kallai, 1978). Thus, reproducibility of the benzidine reaction with clays may depend upon the standardization of methods of clay preparation and storage.

The quantity of benzidine oxidized on Na^+ -montmorillonite was greater than on the Ca^{2+} -form, with 100 mg of clay in 250 ml of 4.1×10^{-5} M benzidine adsorbing 10.3 meq/100 g of semiquinone after one day. However, a sizeable portion of this oxidation must have been due to O_2 rather than Fe^{3+} , since the presence of 2.5 ml of 10^{-1} M NaOH in this system reduced the adsorption to 3.9 meq/100 g. The use of N_2 flow to reduce contact with oxygen also reduced the oxidation-adsorption reaction. These results lend further support to the concept that a dispersed clay (Na^+ -form) with a very large surface area exposed to solution (and dissolved O_2) is more effective in the promotion of oxidation than an aggregated clay (Ca^{2+} -form).

ESR and UV-visible spectra of adsorbed benzidine-

The ESR spectra of the blue (wet) and yellow (air-dry) forms of the benzidine- Mg^{2+} -hectorite complex are shown in Figures 2A and 2B. Little or no free radical signal appeared at $g = 2.00$ for the wet (faintly blue) clay film, although a strong signal was produced by drying the film to produce a bright yellow color (Figure 2C). This signal showed evidence of anisotropic hyperfine splitting, indicating orientation of the radical cation relative to the clay mineral surface (Figure 3). A comparison of signal intensities also shows that the Mg^{2+} -hectorite appears to form more radicals in the dry state than untreated hectorite. This is most likely a result of the acidity required for creation of the divalent "semiquinone" cation (Theng, 1974). The acidity is provided by exchangeable Mg^{2+} , whereas the untreated hectorite is alkaline in nature.

Wet Upton Mg^{2+} -montmorillonite, unlike hectorite, had a strong free radical signal after wetting in a saturated benzidine solution and turning dark blue. Upon

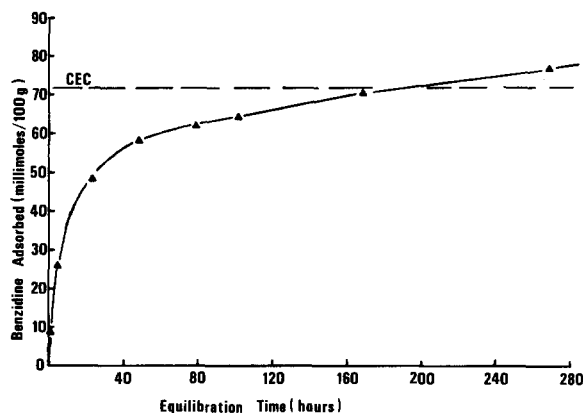


Figure 4. The time-dependent adsorption of benzidine on Cu^{2+} -hectorite. (The CEC is shown by the broken line, indicating the maximum quantity of benzidine-blue cations that could be adsorbed by ion exchange.)

drying to the bright yellow form, most of this signal was lost. These results imply that the lack of signal in the wet Mg^{2+} -hectorite (faint blue) may simply have been due to the very small concentration of benzidine radical cations produced, since Fe^{3+} -hectorite produced a pronounced green color when wetted in benzidine solution and showed a strong free radical signal with ~ 2 gauss linewidth.

The changes in free radical signal observed upon drying the clays are more difficult to explain. It has been proposed that the yellow benzidine species is the divalent "semiquinone" cation (Dodd and Ray, 1960), or alternatively, the divalent quinoidal cation (Hakusui *et al.*, 1970). Since the latter ion is *not* a radical, it is an unlikely product in the case of the yellow form of Mg^{2+} -hectorite, because the ESR signal enhancement upon drying indicates that a semiquinone (radical) has formed. The signal reduced in intensity over several days as the yellow clay converted to a grey color. The drying process, by enhancing protonation of surface-adsorbed molecules (Mortland and Raman, 1968), must shift the equilibrium on these clays strongly toward a yellow product. In fact, the enhancement of signal that accompanies drying of the hectorite may be an indication that neutral benzidine molecules present in the clay are oxidized upon drying, as exposure to O_2 upon removal of water promotes oxidation of excess benzidine. Thus, many more molecules than those present as benzidine-blue may be converted to divalent cations.

Since the radical signal observed in the wet Mg^{2+} -montmorillonite-benzidine complex was greatly reduced in the dry (yellow) form of the clay, the quinoidal product may dominate upon drying. The reason for the different behavior of the two clays is not clear, although high surface concentrations of divalent radicals formed by protonation of the benzidine-blue may be unstable,

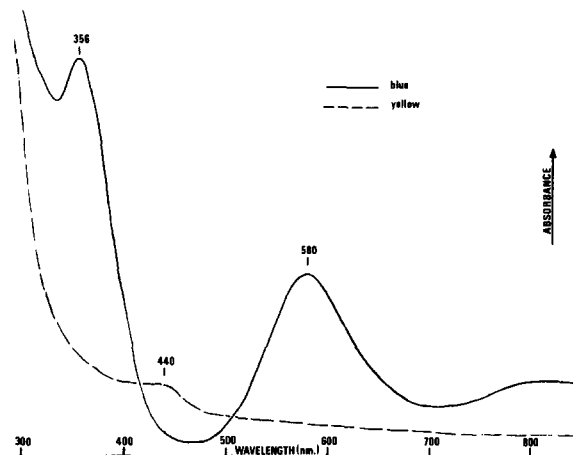


Figure 5. UV-visible spectra of blue and yellow benzidine-montmorillonite complexes in an aqueous suspension with initial benzidine concentration of 4.1×10^{-4} M.

immediately oxidizing further to the quinoidal ion. Possibly, the presence of larger amounts of structural Fe^{3+} expedites the oxidation. Consideration of resonance structures indicates that the yellow divalent radical should be much less stable than the benzidine-blue cation.

Clays, such as Fe^{3+} - and Cu^{2+} -hectorite which oxidized large quantities of benzidine, becoming very deep blue in the process, did not convert completely to the yellow form upon drying. This effect has been observed before (Lahav and Anderson, 1973) and is probably caused by the exchange of metal cations by adsorbed semiquinone cations, thereby greatly reducing clay surface acidity and preventing the proton-dependent conversion of the semiquinone to the divalent cation. The equilibration of Cu^{2+} -saturated hectorite (0.015 g) with 400 ml of 4.1×10^{-5} M aqueous benzidine solution for several days indicated a rapid initial oxidation and adsorption of benzidine-blue cations, with a leveling off of adsorption near the CEC level (Figure 4). Evidently, most of the benzidine in this case was oxidized by Cu^{2+} , since the level of radical cation formation (from ESR spectra) was much higher than in Mg^{2+} -hectorite. After about 20 days of equilibration, almost 90 meq/100 g of benzidine had been adsorbed, suggesting that adsorption by intercalation had occurred beyond the CEC. In addition, the quantity of adsorption that occurred above the CEC of the hectorite was linearly related to the square root of time. This may be an indication that O_2 acted as the oxidizing agent after all of Cu^{2+} had been reduced, and that the rate of the reaction was then determined by diffusion of O_2 to the clay.

The UV-visible spectra of the blue and yellow benzidine-montmorillonite complexes (Figure 5) show a strong absorbance of the blue form at 580 and 356 nm, and a weak absorbance of the yellow complex near 440

nm. The yellow form was created by adding a few drops of 0.1 N HCl to the blue complex, although initially a faintly pink color was evident until the yellow color developed fully. The blue-yellow conversion can therefore be induced by addition of acid to suspension, drying (if a cation capable of generating acidity is present on the clay surface), and even freezing (Lahav and Anderson, 1973). All of these processes provide protons for the conversion of the blue radical cation to the yellow radical cation, but there is some evidence that the absorbed yellow form tends to oxidize further in air to nonradical species.

CONCLUSION

The structural iron content of hectorite, although low, can probably account for the slight initial activity of this clay in forming benzidine-blue. Iron oxide impurities in the hectorite in the form of separate particles and surface coatings showed no significant activity in the oxidation of benzidine. However, the surface-adsorbed hydrated (or partially hydrolyzed) metals, Fe^{3+} and Cu^{2+} , had a high degree of activity in forming the semiquinone cation on the clay. Hectorite (and other expanding phyllosilicate clays) appears to have the unique ability of adsorbing and stabilizing the planar 'semiquinone' cation radical, while in solution the oxidation reaction continues through to the chemically more stable quinoidal product. Electron spin resonance demonstrated that the yellow form obtained upon drying benzidine-treated hectorite is also a radical, probably the divalent cation form. Longer equilibrations of clays with benzidine showed that O_2 oxidation of benzidine became significant, although high pH inhibited this reaction.

The results could be explained without postulating a reaction at clay-edge aluminum sites. Quantitative studies showed that the very small quantities of benzidine-blue cations formed on most natural clays required the reduction of only a small fraction of structural iron. Since the oxidation state of structural iron is sensitive to pretreatment, the exact experimental procedure may greatly influence the degree of color formation when benzidine is added to clay.

ACKNOWLEDGMENTS

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Резюме—С использованием электронного спинного резонанса и ультрафиолетовой видимой спектроскопии определялась роль различных форм примесей Fe(III) в гекторите в связи с окислением бензидина в водной суспензии. Естественное поверхностно-адсорбированное Fe(III) не показало определяемой активности в окислительном процессе, в то время как очень малые количества структурного октаэдрического Fe(III) повидимому способствовали относительно быстрому переходу в радикальный катион. Однако, крайне малые количества бензидина были окислены в сравнении с обменной способностью глины. Недавно адсорбированные катионы Fe³⁺ эффективно окисляли бензидин, но со временем теряли значительно эту способность. Переход электрона от Fe(III) к бензидину отмечался реакцией O₂-бензидин, так как последняя реакция протекала медленно и ограничивалась скоростью диффузии O₂ в систему глина-вода. Реакция O₂-бензидин также задерживалась высоким pH. Существование двух реакционных механизмов и вовлечение только малой части всего структурного железа, как показано сравнением гекторита и монтмориллонита, может объяснить противоречащие интерпретации в литературе. Реакция окисления бензидина требует не только окислителя для формирования радикала, но также поверхность глины, чтобы адсорбировать и стабилизировать его против дальнейшего окисления.

Resümee—Die Rollen von verschiedenen Arten von Fe(III) Verunreinigungen in einem Hektoriten mit Hinsicht auf die Oxydierung von Benzidin in wäßrigen Suspensionen sind mittels Elektronenspin Resonanz und UV-sichtbarer Spektroskopie evaluiert worden. Natürliches Oberflächen adsorbiertes Fe(III) zeigte keine feststellbare Aktivität in dem Oxydierungsvorgang, wohingegen sehr kleine Mengen von strukturellem, oktahedrischem Fe(III) offensichtlich einen relativ schnellen Übergang zu dem radikalen Kation förderte. Im Vergleich zur Austauschkapazität des Tons jedoch, wurden äußerst kleine Mengen von Benzidin oxydiert. Neu adsorbierte Fe³⁺ Kationen oxydieren Benzidin sehr effektiv, aber wenn gealtert, verlieren einen großen Teil dieser Fähigkeit. Die Übertragung von Elektronen zwischen Fe(III) und Benzidin konnte von einer O₂-Benzidin Reaktion unterschieden werden, weil die letztere Reaktion langsam war und durch die Geschwindigkeit der O₂-Diffusion in das Ton-Wasser System begrenzt war. Die O₂-Benzidin Reaktion wurde auch bei hohem pH unterdrückt. Die Existenz zweier Reaktionsmechanismen und die Beteiligung nur eines kleinen Anteils des gesamten strukturellen Eisens, gezeigt durch Vergleich eines Hektoriten und Montmorilloniten, könnte die widersprechenden Auswertungen in der Literatur erklären. Die Benzidin-Blau Reaktion erfordert nicht nur ein Oxydierungsmittel für die Formierung des Radikals, sondern auch eine Tonoberfläche für die Adsorption und um es gegen weitere Oxydation zu schützen.

Résumé—Les rôles des différentes formes d'impuretés de Fe(III) dans une hectorite par rapport à l'oxydation de benzidine en suspension aqueuse ont été évalués utilisant la résonance de spin d'électrons et la spectroscopie à l'UV-visible. Le Fe(III) naturel adsorbé à la surface ne montrait aucune activité détectable dans le procédé d'oxydation, tandis que de très petites quantités de Fe(III) à réseau octaédrique apparemment promeuvent une conversion relativement rapide au cation radical. D'extrêmement petites quantités de benzidine, cependant, ont été oxydées en comparaison avec la capacité d'échange de l'argile. Les cations Fe³⁺ fraîchement adsorbés ont effectivement oxydé la benzidine, mais ont perdu beaucoup de cette aptitude en vieillissant. Le transfert d'électrons Fe(III)-benzidine pouvait être distingué d'une réaction O₂-benzidine, puisque cette dernière était lente et limitée par l'allure de diffusion de O₂ dans le système argile-eau. La réaction O₂-benzidine était aussi inhibée par un pH élevé. L'existence de 2 mécanismes de réaction et l'implication d'une petite fraction seulement de tout le fer structuré, comme le montre la comparaison entre l'hectorite et une montmorillonite, peut expliquer les interprétations contradictoires dans la littérature. La réaction de benzidine bleue exige non seulement un agent oxydant pour former le radical, mais aussi une surface argilleuse pour l'adsorber et le stabiliser face à une oxydation ultérieure.