MECHANISMS OF FORMATION OF COLORED CLAY-ORGANIC COMPLEXES. A REVIEW

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(Received 25 March 1971)

Abstract — The interactions of clay minerals with organic compounds which give rise to the formation of colored complexes, are discussed. The color reactions of clays can be ascribed to a charge transfer between the mineral and the adsorbed species. The active sites on the clay are aluminums exposed at crystal edges and/or transition metal cations in the higher valency state at planar surfaces both of which can act as electron acceptors. The pH of the system, the nature of the solvent and that of the exchangeable cation, influence the rate of color development and the final intensity and quality of the color produced. Steric factors also play a part in reactions involving bulky organics. Some practical applications based on color reactions of clays with electron-donating organic substances are described.

INTRODUCTION

The ability of clays to transform certain organic compounds into colored derivatives has been recognized for some considerable time (see Grim, 1968 for selected bibliography). The benzidine blue reaction of layer lattice minerals is perhaps the best known example of this type of clay-organic interactions. Such systems have for many years been the subject of active interest because of their possible analytical and industrial applications. Information on this segment of clay research, however, is scattered and conflicting views have been expressed as to the nature and location of the sites at the clay surface which are responsible for color formation.

Although gaps still exist in our understanding of the color reactions of clay minerals, significant progress has been made in this area over the past few years and a coherent pattern of these systems is gradually coming to light.

INFLUENCE OF CLAYS ON COLOR REACTIONS

It has been known for many years that the adsorption of certain organic compounds by clays gives rise to the formation of colored complexes (Hauser and Leggett, 1940; Krüger and Oberlies, 1941; Meunier, 1942; Zechmeister and Sandoval, 1945). This observation was ascribed to either acid–base interactions or to oxidation–reduction reactions (Weil-Malherbe and Weiss, 1948). The former situation obtains with acid-washed clays acting as proton donors (Brønsted acids) since the activity of the mineral can largely be suppressed by treatment with a base, such as ammonia. Oxidation–reduction reactions, on the other hand, are little influenced by either acid or base pretreatment of the clay. In this instance, the operative mechanism is one of electron transfer from the adsorbed species to the clay acting as an electron acceptor (Lewis acid). Following Briegleb (1961) such associations between clays and organic compounds may be described as electron-donor–acceptor complexes.

Cation exchanged clays when dried to a low water content (5–6% of the oven-dry weight) can also behave as strong Brønsted acids, the reactive protons deriving from the dissociation of residual water molecules due to the polarization by the exchangeable cations (Fripiat, 1964; Mortland, 1968). This type of acidity besides being dependent on the water content as well as the nature of the exchangeable cation and basicity of the interacting molecules, is also influenced by the solvent. The proton-donating ability of the "dry" clay surface may be estimated by (1) adsorption of ammonia and organic bases and measuring the amount of the corresponding protonated species formed (Mortland, 1970), and (2) by titration in liquid hydrocarbon medium of the clay with organic bases in the presence of Hammett indicators (Walling, 1950; Benesi, 1956, 1967). Such measurements have indicated that the acidity of the clay surface is much greater than would be expected from the pH of its corresponding aqueous suspension, that is, the dissociation constant of the residual water molecules is considerably higher than that of bulk water (Fripiat, Jelli, Poncelet and André, 1965).

In the color reactions of clays with organic molecules, both Lewis and Brønsted acidity are involved and in some instances it is difficult to distinguish between them clearly. In recognizing this fact together with the importance of crystal edges
as electron-accepting sites in these systems, Solomon, Loft and Swift (1968a, 1968b) have provided the key to our understanding of the influence of clay minerals on color reactions. The model which has emerged from their studies is based on charge transfer between the mineral and the adsorbed organic species.

**Charge transfer reactions at crystal edges**

The interaction of benzidine with clays provides an outstanding example of a color reaction activated by layer lattice silicates. The transformation of the colorless diamine to its blue derivative when brought together with certain clays in an aqueous environment, was reported by Hauser and Leggett (1940) and by Hendricks and Alexander (1940). This observation has since been substantiated and confirmed by a number of workers (Endell, Zorn and Hofmann, 1941; Meunier, 1943; Bozassa, 1944; Weil-Malherbe and Weiss, 1948; Vedeneeva, 1950).

The sole feature of the benzidine blue reaction on which agreement is general is that the reaction involves the transfer of an electron (oxidation) from the diamine (Fig. 1a) to the clay to give the blue monovalent radical-cation ("semiquinone"). Conjugation of the unpaired 2pz electron from nitrogen with the π electron system of the aromatic ring and resonance involving both rings account for its stability and blue color (see Fig. 1b). Following an earlier suggestion by Weiss (1938), Dodd and Ray (1960) have pointed out that the monovalent species exists only in a limited range of pH on the acid side of neutrality, accepting a proton on the lone pair of electrons of the nitrogen atom when the pH of the medium falls below 2 to yield the yellow divalent radical-cation (Fig. 1c). The color of the divalent species suggests that the number of resonance structures possible, is limited.

More than three decades ago, Hendricks and Alexander (1940) noted that kaolinite type clays, as opposed to the smectites, failed to give the blue color with benzidine and suggested that, in the absence of organic matter, the benzidine reaction might be used to characterize the montmorillonite group of minerals. Similar observations were reported by Bozassa (1944) and by Vedeneeva (1950). On the other hand, Hauser and Leggett (1940) and Weil-Malherbe and Weiss (1948) observed that their kaolin specimens reacted positively although the color intensity was much reduced as compared with that obtained for bentonite.

In re-examining the benzidine reaction of a number of soils and clays, Page (1941) has pointed out that color formation could equally be brought about by simple inorganic oxidants. Besides organic matter, the presence of such materials as "impurities" in a given clay sample would interfere with color development by masking the activity that the clay itself might possess and hence limit the usefulness of the benzidine blue test as a diagnostic criterion for the smectite group of minerals.

Subsequently, Solomon et al. (1968a) using a range of representative clay minerals showed that, with the exception of talc, each clay specimen gave a blue color of varying intensity when mixed with a (saturated) aqueous solution of benzidine hydrochloride. Pretreatment of the clays with polyphosphate which specifically adsorbs at crystal edge surfaces (Michaels, 1958) caused a marked reduction in the color intensity of the complexes with montmorillonite, hectorite, and nontronite whereas kaolinite and pyrophyllite failed to react altogether.

These observations have led Solomon et al. (1968a) to postulate the presence of oxidizing sites at edge surfaces. These sites consist of the aluminums in octahedral coordination exposed at the

![Fig. 1. Transformation of benzidine into its colored radical-cation forms activated by clays.](image-url)
crystal edges acting as electron acceptors (Lewis acids). Their data also show that edge aluminums are responsible for all of the activity of kaolinite and pyrophyllite toward benzidine whereas the smectite minerals possess oxidizing sites elsewhere within the crystal lattice in addition to those located at the edges.

**Charge transfer reactions at planar surfaces**

Hendricks and Alexander (1940) have hinted that ferric iron forming a part of the montmorillonite lattice might act as an oxidizing agent in the benzidine reaction. In following up this suggestion, Page (1941) proposed that ferric ions exposed at broken crystal edges would be capable of being reduced, that is, of accepting electrons and so contribute to color formation. More definite evidence for the part played by lattice-bound ferric ions was provided by Weil-Malherbe and Weiss (1948) who showed that reduction of their reactive clay samples with stannous chloride inhibited color development whilst no effect of this kind was observed by the mere removal of "loosely-bound" iron using conventional extractants. Similarly, Bloch, Charbonnelle and Kayser (1953) reported that lattice ferric ions were involved in the oxidation of benzidine by montmorillonite. Earlier, Krüger and Oberlies (1943) observed a striking enhancement in the intensity of the blue color of their montmorillonite-benzidine complexes by preheating the minerals in air at 100°C, indicating that an oxidation-reduction mechanism was involved in color formation.

It is left to Solomon et al. (1968a, 1968b), however, to demonstrate unambiguously that ferric ions occupying octahedral sites within the silicate layers, exert a profound influence on the color reactions of clays. These cations accept electrons from the adsorbed organic molecules and so convert to the ferrous state although the precise mechanism as to how this occurs is incompletely understood. Thus the increase and decrease in color intensity of montmorillonite complexes brought about by oxidation (e.g. heating in air) and by reduction (e.g. treatment with hydrazine) of the mineral, respectively, are accompanied by a corresponding change in the valency state of the iron. This change is indicated by an enhancement of the signal for ferric ion in the ESR spectrum of the oxidized clay and by increases in the cation exchange capacity and ferrous iron content of the reduced mineral. Since the iron is located in the interior of the crystal lattice—apart from the few exposed at the edges—the activity of the clay, in this instance, may be ascribed to the planar surfaces.

Montmorillonite type minerals clearly possess both "crystal edge" and "planar surface" activity since treatments to deactivate either the edge surfaces (by adsorption of polyphosphate) or the planar surfaces (by reduction) fail to suppress color development entirely. However, reduction of the clay followed by treatment with polyphosphate completely inhibits the activity of montmorillonite. It is of interest to note that the polyphosphate treated hectorite specimen used by Solomon et al. (1968a) gave a (very pale) blue color with benzidine. This observation would not be anticipated from the "ideal" hectorite structure (Grim, 1968). Although the presence of extraneous ferric compounds could not be excluded, it would appear that their sample contained some ferric ions replacing magnesium or lithium in octahedral positions.

It is evident that the charge transfer theory can account for the variations in the activity of different clay minerals toward benzidine. All things being equal, the color intensity of the clay-benzidine complex is dependent on the number of active (electron-accepting) centers in the mineral and their relative distribution between crystal edges and planar surfaces each or both of which may be altered by simple chemical treatments.

**FACTORS AFFECTING COLOR FORMATION**

The reaction of layer lattice minerals with benzidine is discussed at some length because it typifies those interactions of clays with organic compounds which give rise to a color change of the adsorbed species. Besides benzidine, a large number of organics (mainly aromatic amines) are capable of forming electron-donor-acceptor complexes with clay minerals producing a wide variety of colors (Hauser and Leggett, 1940; Hendricks and Alexander, 1940; Meunier, 1943; Dodd, 1955; Dodd and Ray, 1960; Solomon et al., 1968b). There are, however, instances when deviations from the benzidine model occur. These are due to factors which influence the ability of the organic molecule to effect a close approach of the silicate surface.

**pH and solvent**

Using a series of aqueous buffer solutions (pH 0.5-6.5), Dodd and Ray (1960) noted that the amount of benzidine (expressed as moles per unit weight of clay) adsorbed by montmorillonite and hectorite increased with a rise in pH. Since pH controls the charge on the diamine (Fig. 1), their data accord with the adsorption process being essentially one of exchange of the benzidine radical-cation for the inorganic cation initially present at the clay surface. It is also evident from Fig. 1 that the color of the complex is dependent on the pH of the system. From visual examination of their complexes, Dodd and Ray (1960) deduced that only the divalent radical-cation was adsorbed be-
between pH 0.5 and 1.5. At pH 4.2 the monovalent ion alone was present at the surface whilst a mixture of both species existed in the intermediate range of pH.

As pointed out earlier, the acidity of the system may be substantially increased by drying the mineral since this promotes the dissociation of the residual water molecules. This increase in Brønsted acidity provides an explanation as to why a yellow complex is obtained when an anhydrous benzene (or ethanol or acetone) solution of benzidine is added to "dry" montmorillonite (Takahashi, 1955; Hasegawa, 1961; Solomon et al., 1968a) and why the blue complex turns yellow when strong acid is added (Solomon et al., 1968a) or water is removed (Vedeneeva, 1950; Takahashi, 1955). Conversely, the blue color of the complex may be restored by addition of water to its benzene suspension or by allowing the yellow complex to take up water vapor (Takahashi, 1955; Solomon et al., 1968a). Following Dodd and Ray (1960) the role of water in these systems may therefore be represented by the following equation (compare Fig. 1b and c),

$$M - B^+ + H_2O^+ \rightleftharpoons M - B^{2+} + H_2O$$

where M and B refer to montmorillonite and benzidine, respectively.

The influence of water extends beyond that of acting as a proton acceptor (equation). It has been shown by several workers (Greene-Kelly, 1955; Takahashi, 1955; Haxaire and Bloch, 1956) that benzidine is capable of forming an interlayer complex with montmorillonite when adsorbed from an aqueous solution. The water presumably acts as a swelling agent facilitating the entry of benzidine into the interlayer space. On the other hand, benzene is not normally intercalated by montmorillonite (Greene-Kelly, 1955). This limits the access of the interlayer regions to benzidine when benzene is used as the solvent so that adsorption is primarily confined to external crystal surfaces. A notable exception, equally relevant to the present discussion, is the behavior of Cu(II)–montmorillonite which does form an interlayer colored complex with benzene (Doner and Mortland, 1969). In this instance the benzene molecule donates its π electrons to the Cu(II) ion (π bonding). Using i.r. spectroscopy, Mortland and Pinnavaia (1971) have demonstrated that two types of interlayer π complexes are formed depending on the degree of hydration of the mineral. The complex in which benzene is bound to a partially hydrated Cu(II) ion is green in color whilst a red complex is obtained when a thoroughly degassed clay sample is exposed to benzene vapor. Like the blue–yellow transition in complexes with benzidine, the red and green forms of Cu(II) montmorillonite–benzene complexes are readily interconvertible by varying the water content of the system.

We have already noted that benzidine forms a yellow complex with dry montmorillonite irrespective of whether benzene or ethanol is used as the solvent. This behavior contrasts with that of the stable reddish-purple free radical, 2,2-diphenylpicrylhydrazyl (DPPH'), and of some leuco dyes (e.g. leuco malachite green) both of which react with dry montmorillonite in an anhydrous benzene environment but fail to do so when ethanol is substituted for benzene (Solomon et al., 1968b). Thus a benzene solution of DPPH' (Fig. 2) is decolorized...
and the leuco base attains the characteristic color of its oxidized form when brought into contact with clays capable of accepting electrons.

Solomon et al. (1968b) rationalize the data by postulating that ethanol, being a stronger Lewis base (electron donor), is preferentially adsorbed over DPPH and the leuco dyes which are thereby prevented from approaching the Lewis acid sites at the clay surface. Benzidine, on the other hand, competes successfully with ethanol (and water) for the active centers and complex formation occurs. It ought, perhaps, to be interpolated at this point, that DPPH is a weak electron acceptor and is used as such in organic analysis (Paperiello and Janish, 1966). That it behaves as a reducing agent (electron donor) rather than as an oxidant in these systems must be because the (oxidized) clay is a stronger electron acceptor. It is indeed possible for the roles to be reversed, that is, for the mineral to act as an electron donor when the organic with which it forms a complex has strong electron-accepting properties. Such a situation is encountered in the reaction of reduced montmorillonite with tetracyanoethylene (TCNE). Here, the organic species accepts an electron from ferrous ion (Fig. 3) at the planar surface to yield a red radical-anion (Solomon et al., 1968b). An analogous mechanism has been shown to operate in the reduction of TCNE by dehydrated alumina catalysts (Flockhart, Leith and Pink, 1969).

Nature of the exchangeable cation

In reactions involving expanding layer lattice minerals, the exchangeable cations influence color formation in so far as they control the extent of crystalline (interlayer) swelling in water of the clay, and hence, the rate at which the organic compound enters the interlayer regions. Norrish (1954) has demonstrated that sodium montmorillonite shows extensive crystalline swelling in water whereas the calcium clay does not expand beyond a basal spacing of 19 Å. The final intensity of the blue color which develops when an aqueous solution of benzidine is added to montmorillonite is accordingly more rapidly attained with the sodium than with the calcium saturated mineral (Solomon et al., 1968a). The available evidence suggests that in systems involving benzidine and organics of similar size and compactness, the exchangeable cations (even if these are of the transition metal type) only influence the rate of color formation but have little effect on the amount of organic adsorbed (Dodd and Ray, 1960).

On the other hand, transition metal cations occupying exchange positions play an active part in color reactions involving bulky organics which for steric reasons are incapable of undergoing charge transfer reactions at planar surfaces. For example, DPPH normally reacts at crystal edges presumably because these superficially located sites can be more closely approached than those centers “buried” within the silicate layers. Thus calcium montmorillonite which has previously been treated with polyphosphate to coat the crystal edges, fails to decolorize a benzene solution of DPPH whereas a similarly treated cobalt saturated clay only shows a reduced activity. Solomon et al. (1968b) suggested that the cobalt ion acted as a “bridge” across which an electron from DPPH was transferred to a ferric ion at the planar surface (Fig. 2).

Benzidine, however, is capable of participating directly in charge transfer reactions at both crystal edges and planar surfaces because its size and shape evidently allow it to effect close contact with the clay surface. For this reasons, the nature of the exchangeable cation has but little influence on the activity of the clay toward benzidine.

Other factors

Since charge transfer reactions involve the interaction of orbitals it seems probable that the orientation of the adsorbed species at the clay surface plays an important part in these systems. Although a favorable orientation is implied in the general theory of Solomon et al. (1968a, b), orientation effects have largely been omitted from discussion of color reactions in general. Vedeneeva (1950) made reference to such effects when he related the activity of certain clays to the distance separating

\[
\begin{align*}
\text{NC} & \equiv \text{Cl} \equiv \text{CN} + \text{Fe}^{++} \rightarrow \text{NC} \equiv \text{C} \equiv \text{CN} \\
\text{Tetracyanoethylene (TCNE)} & \quad \text{Planar surface} \\
\text{NC} & \equiv \text{Cl} \equiv \text{CN} + \text{Fe}^{++} \\
\text{Tetracyanoethylene radical-anion (red)} & \quad \text{Planar surface}
\end{align*}
\]

Fig. 3. Reduction of tetracyanoethylene (TCNE) to its radical-anion by (reduced) clays.
the amino groups in the benzidine molecule. The orientation imposed on the organic compound by the clay surface, particularly when interlayer complex formation is involved, clearly warrants further investigation.

The oxidation of organic compounds at clay surfaces frequently gives rise to different end products depending on the type of mineral used. Thus the reaction of dimethylaniline with kaolinite and asbestos yielded crystal violet whereas that with montmorillonite possibly gave rise to a derivative of tetramethylbenzidine (Krüger and Oberlies, 1941; Solomon et al., 1968b). No adequate explanation has been advanced to account for these observations since many variables are involved in the adsorption process. Clearly, the nature and location of the active centers—crystal edges in kaolinite and mainly planar surfaces in montmorillonite—as well as orientation factors referred to above, must contribute to the manner in which the activated organic species reacts further at the clay surface. It is therefore difficult, in many instances, to identify the reaction products unequivocally. Moreover, clay-organic complexes, particularly those involving aromatic amines, are susceptible to further oxidation by atmospheric oxygen (White and Cowan, 1960; Weiss, 1963). This fact coupled with difficulties encountered in the extraction and isolation of the colored pigments from their respective complexes (Bloch and Kayser, 1953) introduce an additional uncertainty into the analysis of the reaction products.

**SOME PRACTICAL APPLICATIONS**

Hendricks and Alexander (1940) were the first to advocate the use of the benzidine reaction as a (qualitative) test for characterizing the smectite group of clay minerals. The preceding discussion makes it clear that the test, as originally proposed, is only of limited application (Page, 1941). However, with a few simple modifications (e.g. heating the sample in air followed by washing with polyphosphate), the benzidine blue test may still serve as a useful diagnostic criterion for the presence or absence of montmorillonite type minerals. Similarly, the staining tests proposed by Mielenz and King (1951) are based on the development of certain colors when a series of color-forming organics are reacted with clays under prescribed conditions, e.g. the yellow color formed when montmorillonite is brought into contact with benzidine at pH 1. Since Hendricks and Alexander’s paper (1940), however, other equally rapid and more reliable methods of clay mineral identification have been developed (Brown, 1961). These methods together with the general availability of modern analytical instruments have largely supplanted those tests which are based on color formation involving specified organic compounds.

The color reactions of clays enjoy substantial application for the manufacture of pressure-sensitive carbon-free paper. The chemistry of the process is based on bringing together a suitable electron-donating organic substance and a clay capable of accepting electrons when pressure is applied (Green, 1950; Kranz, 1963; also patents taken out by the National Cash Register Company, 1963; 1965). A variant of this process is the production of light-fast colored printing paper. In this instance, the organic compound (e.g. triphenyl methane) is allowed to react with the clay present as a coating on the paper. This markedly increases the stability of the dye slowing down its decomposition by light (Ritzerfeld and Ritzerfeld, 1961).

Oxidation-reduction reactions based on charge transfer between organic molecules have been used in the determination of “electron-rich” compounds because the formation of electron-donor–acceptor complexes gives rise to characteristic charge transfer bands (Schenk, 1968). The use of clay minerals as electron-donating or electron-accepting agents in organic analysis has not been fully explored although Hasegawa (1961; 1962; 1963) has indicated their potential. Complex formation involving DPPH and TCNE, for example, could be used to indicate the number as well as the location of the active sites in the clay by measuring the concomitant change in the intensity of the color and/or of the signal due to the organic radical in the ESR spectrum (Solomon et al., 1968b; Flockhart et al., 1969).

**CONCLUSION**

The principal contribution of the charge transfer theory lies in the fact that it takes cognizance of the importance of the crystal edges as electron-accepting sites in addition to transition metal cations in the higher valency state located at planar surfaces. Equally important is the realization that both Lewis and Brønsted acidity are involved in the color reactions of clays. Although a number of problems await solution, the theory has instilled a considerable measure of order in what previously seemed to be a collection of interesting but somewhat disconnected and, at times, conflicting experimental observations.

It is also clear that the mechanisms underlying the formation of colored clay-organic complexes are analogous to those involved in the polymerization of adsorbed organic monomers by clays (Solomon, 1968; Theng and Walker, 1970). This indicates the wide applicability of the charge transfer theory to the activation of organic species at clay mineral surfaces.
COLORED CLAY-ORGANIC COMPLEXES

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Résumé — Les interactions des minéraux argileux avec les composés organiques qui donnent naissance à la formation de complexes colorés sont discutées. Les réactions colorées avec les argiles peuvent être attribuées à un transfert de charge entre le minéral et l'espèce adsorbée. Les sites actifs de l'argile sont les atomes d'aluminium exposés sur les bords des cristaux, et/ou, les cations métalliques de transition dans un état de valence élevé sur les surfaces basales, chacun d'eux pouvant agir comme accepteur d'électrons. Le pH du système, la nature du solvant et celle du cation échangeable, influencent la vitesse du développement de la coloration, et l'intensité et la qualité finales de la teinte produite. Des facteurs stériques jouent également un rôle dans les réactions se produisant avec les composés organiques encombrants. Un certain nombre d'applications pratiques fondées sur les réactions colorées des argiles avec les composés organiques donneurs d'électrons sont décrites.


Резюме — Обсуждается характер взаимодействия глинистых минералов с органическими соединениями, которое приводит к образованию окрашенных комплексов. Цветная реакция глин может быть приписана перемещению заряда между минералом и адсорбированным веществом. Активными центрами на поверхности глины являются атомы алюминия, выходящие на грани кристаллов и/или катионы переходных металлов в высоко валентном состоянии на плоских поверхностях; оба типа центров могут вести себя как акцепторы электронов. На скорость появления окраски, ее конечную интенсивность и характер влияют pH системы, природа растворителя и обменных катионов. Стерические факторы также играют роль при реакциях с объемными органическими молекулами. Описаны некоторые примеры практического применения методики, основанного на цветных реакциях глин с электронно-донорными органическими соединениями.