

## 436. Colour Reactions and Adsorption of Some Aluminosilicates.

By H. WEIL-MALHERBE and J. WEISS.

It is known that a number of substances such as aromatic amines and vitamin-A produce deep colours on certain aluminosilicate minerals. These phenomena have been investigated and it has been found that two different mechanisms are responsible for this.

Reactions similar to that of vitamin-A can be produced with other molecules possessing a system of conjugated double bonds, and these colour reactions are observed only if the aluminosilicate possesses the functions of an acid. It is thus closely related to the phenomenon of "halochromy" and is due to the formation of salt-like surface compounds, the conjugated system acting as base. In the case of benzidine and related substances the colours produced are due to the oxidative formation of radicals by certain metal ions of the crystal lattice (*e.g.*, Fe<sup>3+</sup>). The corresponding adsorption isotherms have been investigated in some detail. The significance of these reactions for the catalytic action of aluminosilicates is discussed.

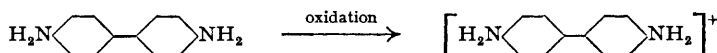
In recent years a number of colour reactions attendant upon the adsorption of various substances on aluminosilicate minerals have been described, particularly those produced by benzidine and other aromatic amines (Hauser and Leggett, *J. Amer. Chem. Soc.*, 1940, **62**, 1811; Krüger and Oberlies, *Ber.*, 1941, **74**, 1711; *Naturwiss.*, 1943, **31**, 92) and those produced by vitamin-A and other carotenoids (*cf.* Meunier, *Bull. Soc. chim.*, 1946, **13**, 73, 77). However, no clear distinction between these various groups of colour reactions has been made, and little is known about the mechanism of colour formation. We have investigated the ability of some silicate minerals to produce coloured adsorption compounds and, as a result, a classification of these phenomena now seems possible. In addition, the adsorption isotherms of colour-producing and non-colour-producing systems were studied.

Aluminosilicates which occur in Nature as various clays are of great importance as catalysts, *e.g.*, in the isomerisation and cracking of hydrocarbons. Since our results contribute to the understanding of the chemical reactivity of these compounds, they may also have some bearing on their catalytic action.

(1) *Colour Reactions.*—Our results indicate that there are two mechanisms underlying colour formation :

(i, a) In the first group, colour formation is presumably due to an acid-base type of reaction. Substances which are known to give deep colours with strong acids such as concentrated sulphuric acid (*cf.* Hammett, "Organic Chemistry," McGraw-Hill, 1941) also produce identical or very similar colours upon adsorption on suitable clays. A number of these halochromic substances owe their electron-donating, *i.e.*, basic, properties to a system of conjugated double bonds, *e.g.*, dicinnamylideneacetone, dianisylideneacetone, and similar ketones, and vitamin-A and other carotenoids. Their basic character is, however, so weak that the coloured salts are easily hydrolysed by water. Others, like dimethylaminoazobenzene and other azo-dyes, are stronger bases and are able to form coloured ions even in an aqueous medium. The two classes of compound show an analogous behaviour towards adsorbing clays. As shown in Table I the clays react like acids, and this can be modified by suitable treatments. Pre-treatment with hydrochloric acid usually enhances the intensity of the colour reactions; on the other hand, dicinnamylideneacetone and vitamin-A, which are very weak bases, are no longer chromogenic on ammonia-treated clays. Owing to their stronger basicity, azo-dyes still show the colour of their ions, though with reduced intensity, on clays after ammonia-treatment. The inhibition of the colour reactions by ammonia treatment is reversible by acid treatment and *vice versa*.

(i, b) The colour production in the second group is presumably due to an oxidation-reduction mechanism. An example is the colour reaction of benzidine (Hendricks and Alexander, *J. Amer. Soc. Agron.*, 1940, **32**, 455; Endel, Zorn, and Hofmann, *Angew. Chem.*, 1941, **54**, 376) and of other aromatic amines studied more recently by Krüger and Oberlies (*loc. cit.*) and by Hauser and Leggett (*loc. cit.*). The benzidine-blue reaction is known to be due to the oxidation of benzidine to the univalent benzidine cation (*cf.* Weiss, *Chem. and Ind.*, 1938, **57**, 517) :



We found that the colour reaction of clays with benzidine remained unaffected by pre-treatment of the clays with acids or bases, but it was generally suppressed after the clays had been refluxed with a solution of 10% stannous chloride in concentrated hydrochloric acid. The colour reactions given by the halochromic substances of group (i, a) are unaffected by this treatment.

TABLE I.

## Colour reactions on aluminosilicate clays.\*

Substrates dissolved in benzene (approx. 0.01 mg. per cent. solutions).

Adsorbent.	Benzidine.	Dicinnamylidene- acetone.	Vitamin-A.	Azo-dyes.
A. Untreated clays.				
Clarit .....	+	+	+	+
Fuller's earth .....	+	+	+	+
Bentonite.....	+	-	-	(+)
Montmorillonite .....	(+)	+	+	+
Kaolin .....	(+)	+	+	+
B. After hydrochloric acid treatment.				
Clarit .....	+	+	+	+
Fuller's earth .....	+	+	+	+
Bentonite .....	+	+	+	+
Montmorillonite .....	(+)	+	+	+
Kaolin .....	(+)	+	+	+
C. After ammonia treatment.				
Clarit .....	+	-	-	(+)
Fuller's earth .....	+	-	-	(+)
Bentonite.....	+	-	-	(+)
Montmorillonite .....	(+)	-	-	(+)
Kaolin .....	(+)	-	-	(+)
D. After stannous chloride treatment.				
Clarit .....	-	+	+	+
Fuller's earth .....	-	+	+	+
Bentonite.....	(+)	+	+	+
Montmorillonite .....	-	+	+	+
Kaolin .....	-	+	+	+

\* + positive, (+) weakly positive, - negative.

Our specimens of montmorillonite and kaolin gave only a feeble benzidine reaction, which appeared after several minutes and slowly increased in intensity. This slow development of colour was in marked contrast to the instantaneous reactions observed in group (i, a) and in itself suggests a different reaction mechanism. Stannous chloride treatment completely suppressed the benzidine reaction of these two clays, as also of fuller's earth and clarit; with bentonite only a partial inhibition was obtained. Refluxing with concentrated hydrochloric acid alone or treatment with sodium sulphide and oxalic acid (cf. Dion, *Soil Sci.*, 1944, 58, 711), which is supposed to remove the loosely bound intermicellar iron, had no effect. This suggests that the colour formation, influenced by stannous chloride treatment, is related to lattice-bound oxidising ions, most probably ferric ions, and the assumption is further supported by the analysis of fuller's earth and clarit before and after stannous chloride treatment, showing a decrease of iron content (Table II). It is possible that the remaining iron has been reduced to the inactive ferrous form by stannous chloride.

Heating with concentrated hydrochloric acid in a sealed tube at 150° completely destroyed both the colour-producing properties and the adsorption capacity of all clays. X-Ray analysis of the minerals thus treated showed that their natural structure had disappeared. Colour formation and adsorption therefore depend on the crystallographic structure.

TABLE II.

## Iron content of clays before and after stannous chloride treatment.

Substance.	Treatment.	Fe, %.	Benzidine reaction.
Clarit .....	HCl-treated (refluxed)	1.54	+
	SnCl <sub>2</sub> -treated	0.42	-
Fuller's earth .....	HCl-treated (refluxed)	1.13	+
	SnCl <sub>2</sub> -treated	0.73	-

(2) *Adsorption Properties.*—Since both colour production and adsorption are surface phenomena, their mutual relationship was investigated by determining the adsorption isotherms of systems consisting of a chromogenic substance and an adsorbent clay which was either in a state in which it gave a positive colour reaction or in which the colour production had been

prevented by a suitable treatment. In practically every case the adsorption could be represented by the Freundlich isotherm  $q = \alpha c^n$ , where at equilibrium,  $q$  = millimols. of solute adsorbed per g. of adsorbent,  $c$  = concentration of the solute in the supernatant solution (mol./l), and  $\alpha$  and  $n$  are constants. The value of  $n$  in the above equation was determined graphically from the  $\log q - \log c$  curve; the constancy of the values for  $\alpha$  provides a test for

TABLE III.

*Adsorption isotherms calculated according to the equation  $q = \alpha c^n$ .*

Adsorbent.	Substrate.	Adsorbent, mg.	$10^3 q$ .	$10^3 c$ .	$n$ .	$\alpha$
Bentonite, HCl-treated	Benzidine	7.6	252.3	0.0532	0.101	0.680
		33.2	219.6	0.0158		0.669
		90.4	263.9	0.0956		0.670
		179.9	343.8	1.263		0.673
Fuller's earth (Redhill), SnCl <sub>2</sub> -treated	Benzidine	13.5	117.1	0.232	0.350	2.196
		38.9	147.2	0.452		2.187
		94.9	200.9	1.119		2.173
		177.6	293.3	3.161		2.205
Bentonite, SnCl <sub>2</sub> -treated	AAT *	9.7	96.2	0.258	0.078	0.183
		39.8	100.5	0.555		0.180
		131.0	110.4	1.755		0.181
		148.0	128.2	10.51		0.183
Bentonite, HCl-treated	DCA †	10.1	59.2	0.230	0.131	0.177
		34.7	60.4	0.629		0.159
		76.0	79.1	2.293		0.175
		147.0	89.9	7.842		0.170

\* AAT = 4-Amino-2':3-azotoluene.

† DCA = Dicinnylamylideneacetone.

TABLE IV.

*Constants of the Freundlich adsorption isotherm, and colour formation of some clay minerals.\**

Determination.	AAT.	DCA.	Benzidine.	Determination.	AAT.	DCA.	Benzidine.
Bentonite, untreated.				Fuller's earth (a), NH <sub>3</sub> -treated.			
Colour	(+)			Colour	(+)	—	+
$\alpha$	1.47			$\alpha$	0.073	3.60	2.70
$n$	0.94			$n$	0.25	0.89	0.39
Bentonite, HCl-treated.				Fuller's earth (a), SnCl <sub>2</sub> -treated.			
Colour		+	+	Colour	+		—
$\alpha$		0.170	0.67	$\alpha$	2.00		2.20
$n$		0.13	0.101	$n$	0.64		0.35
Bentonite, NH <sub>3</sub> -treated.				Fuller's earth (b), HCl-treated.			
Colour	(+)	—	+	Colour			+
$\alpha$	0.196	1.42	1.71	$\alpha$			0.50
$n$	0.72	0.668	0.33	$n$			0.062
Bentonite, SnCl <sub>2</sub> -treated.				Fuller's earth (b), NH <sub>3</sub> -treated.			
Colour	+			Colour			+
$\alpha$	0.182			$\alpha$			0.20
$n$	0.078			$n$			0.169
Fuller's earth (a), untreated.				Clarit, HCl-refluxed.			
Colour	+			Colour			+
$\alpha$	0.98			$\alpha$			1.50
$n$	0.42			$n$			0.21
Fuller's earth (a), HCl-treated.				Clarit, SnCl <sub>2</sub> -treated.			
Colour		+	+	Colour			
$\alpha$		1.56	0.90	$\alpha$			5.63
$n$		0.426	0.13	$n$			0.51
Fuller's earth (a), HCl-refluxed.				Montmorillonite, HCl-treated.			
Colour			+	Colour			(+)
$\alpha$			1.33	$\alpha$			1.59
$n$			0.218	$n$			0.25

\* Fuller's earth : (a) from Redhill, Surrey; (b) supplied by British Drug Houses Ltd.

the validity of the adsorption isotherm. The deviations from the mean value of  $\alpha$  were small throughout. Space does not permit the full communication of our results but a few typical examples are reproduced in Table III. In Table IV values of  $\alpha$  and  $n$  for various adsorbents have been correlated with the colour formation.

The adsorption experiments show that adsorption may be relatively strong even when the colour reaction is negative. It is clear, however, from the figures of Table IV that the character of the adsorption isotherm does not remain unaltered by a treatment which destroys the colour reaction. There seems to be a general tendency for both the constants  $\alpha$  and  $n$  to assume low values if the adsorbent is or becomes strongly colour-positive. In order to understand the significance of these changes it is necessary to consider a theoretical interpretation of the Freundlich isotherm. Such treatments have been given by Henry (*Phil. Mag.*, 1922, **44**, 689) and Zeldovitch (*Acta Physicochim. U.S.S.R.*, 1934, **1**, 961). More recently Cremer and Flügge (*Z. physikal. Chem.*, 1938, *B*, **41**, 453) and Halsey and Taylor (*J. Chem. Physics*, 1947, **15**, 624) have discussed this problem. Our own treatment, which was arrived at independently, is practically identical with that of the last-named authors. It can be briefly summarised as follows :

The Langmuir adsorption isotherm for a single type of adsorption location can be expressed in the form given by Fowler (*Proc. Camb. Phil. Soc.*, 1935, **31**, 260) :

$$q_{(a)} = \frac{N_s c A(T) e^{\chi/RT}}{[1 + c A(T) e^{\chi/RT}]} \dots \dots \dots (1)$$

where  $\chi$  denotes the heat of adsorption,  $c$  the concentration of the solute (or pressure in the case of a gas),  $N_s$  the total number of adsorption locations (*e.g.*, per  $\text{cm}^2$  of surface);  $A(T)$  is a function of the temperature (independent of  $\chi$  and  $c$ ) and contains the partition functions of the adsorbed and unadsorbed molecules. For an adsorbent with regions of different adsorption locations one obtains :

$$q = \int_0^\infty \frac{c A(T) e^{\chi/RT}}{[1 + c A(T) e^{\chi/RT}]} N(\chi) d\chi \dots \dots \dots (2)$$

if  $N(\chi)d\chi$  is the number of locations with adsorption energies between  $\chi$  and  $(\chi + d\chi)$ .

Assuming that the adsorption energies follow a Boltzmann distribution given (with the proper normalising factor) by

$$N(\chi)d\chi = (N_s/R\theta) e^{-\chi/R\theta} \cdot d\chi \dots \dots \dots (3)$$

where  $R\theta (= \chi_m)$  can be regarded as the *minimum* mean adsorption energy it can be shown that if this is introduced into equation (2) one obtains finally :

$$q = N_s \frac{RT}{\chi_m} \left\{ (Ac)^{RT/\chi_m} \frac{\pi}{\sin\left(\frac{RT\pi}{\chi_m}\right)} - \frac{(Ac)}{\left(1 - \frac{RT}{\chi_m}\right)} + \frac{(Ac)^2}{\left(2 - \frac{RT}{\chi_m}\right)} - \dots \right\} \dots (4)$$

which for small values of  $(Ac)$  reduces to

$$q \sim \left\{ N_s \frac{RT}{\chi_m} A^{RT/\chi_m} \frac{\pi}{\left(\sin \frac{RT\pi}{\chi_m}\right)} \right\} c^{RT/\chi_m} \dots \dots \dots (5)$$

This is of the same form as the equation of the Freundlich isotherm ( $q = \alpha c^n$ ) if one puts

$$n = RT/\chi_m = T/\theta$$

$$\alpha = N_s \frac{RT}{\chi_m} \frac{\pi}{\left(\sin \frac{RT\pi}{\chi_m}\right)} A^{RT/\chi_m}$$

In general, the smaller the adsorption energy (the smaller  $\chi_m$ ), the greater is the exponent  $n$ . Small values of  $n$  are thus connected with high values of  $\chi_m$ , which means high adsorption energies, *i.e.*, approaching chemisorption and indicating a chemical process on the surface. On the basis of this theoretical interpretation one can conclude that colour formation is connected with adsorption on centres of high adsorption energy probably involving chemical interaction. A value of  $RT/\chi_m$  nearer to unity ( $\chi_m \sim RT$ ) would indicate a predominantly "physical" interaction.

The question is as to how these chemical surface reactions can be explained. The formation of benzidine-blue and the oxidation of aromatic amines is relatively easy to understand, as this is obviously due to an oxidation of the amine by lattice-bound metal ions.

The action of aluminosilicates as strong acids in the halochromic colour reactions is less obvious. It can, however, be understood from certain ideas proposed by Pauling ("The Nature of the Chemical Bond", Cornell University Press, 2nd ed., 1947, p. 396). It is known that the aluminosilicates represent a complete framework of linked tetrahedra involving ( $\text{Si}^{4+}$ ), ( $\text{Al}^{3+}$ ), and ( $\text{O}^{2-}$ ) ions.  $\text{Al}(\text{OH})_3$  and  $\text{Si}(\text{OH})_4$  are very weak acids as the  $\text{O}^{2-}$  is acted upon in each case by a total bond strength of 1 from the central atom thus leaving one full bond strength on the  $\text{O}^-$  atom for the binding of the hydrogen atom. This is different in the aluminosilicates where one has ( $\text{Si}^{4+} \cdot \text{O}^{2-}$ ) tetrahedra with corners shared with  $\text{Al}^{3+}$  tetrahedra. An ( $\text{O}^{2-}$ ) ion which is common to an ( $\text{Al}^{3+}$ ) and an ( $\text{Si}^{4+}$ ) tetrahedron is thus acted upon by a total bond strength of  $(4/4 + 3/4) = 7/4$  bond strengths, leaving only  $(2 - 7/4) = 1/4$  for the binding of the hydrogen atom: thus a strong acid results.

On the basis of this simple picture the strength of this acid should be comparable to that of perchloric acid,  $\text{HClO}_4$ , where each oxygen atom is also held by a bond strength of  $7/4$ . Treatment of an alkali salt of the aluminosilicate with acid will liberate the acid and the surface of the acid-treated clay will become strongly proton-donating.

(3) *The Action of Silica-Alumina Catalysts.*—It is known that silica-alumina catalysts, under suitable conditions, can bring about all the types of chemical reaction which are generally associated with catalysts of the nature of a strong acid (*e.g.*, alkylation, dealkylation, cracking, Friedel-Crafts reactions). It is also known that in these processes the first and essential step is the formation of a positive carbonium ion which is formed, *e.g.*, by the addition of a proton from the catalyst. These positive ions are relatively unstable and undergo characteristic changes leading to the reactions mentioned above (*cf.* Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3276; Hansford, *Ind. Eng. Chem.*, 1947, **39**, 849).

In the case of the silica-alumina catalysts these positive ions are formed on the surface of the catalyst with the protons from the catalyst surface.

It has been shown above that these protons are also responsible for a certain type of colour reaction (*e.g.*, with dicinnamylideneacetone) and it is thus clear that this colour reaction should be a useful indication of the proton-donating properties of the surface and thus of its catalytic activity. Experiments to correlate these two functions are now in progress and will be reported in due course.

#### EXPERIMENTAL.

*Adsorbents used.*—Bentonite was from Wyoming, U.S.A., fuller's earth as noted in Table IV, clarit from Messrs. Lever Bros., montmorillonite from the Rhön Mountains, Germany, and kaolin was a commercial sample of unknown origin, labelled "acid washed".

*Treatment of Adsorbents.*—"HCl-treated": the adsorbent was stirred at room temperature with 50–100 vols. of concentrated acid and centrifuged. The treatment was twice repeated and the adsorbent was finally washed with three changes of distilled water.

"HCl-refluxed": the adsorbent was refluxed for 30–60 mins. with 50–100 vols. of concentrated acid. After cooling, it was washed on the centrifuge first with concentrated hydrochloric acid, then several times with distilled water.  $\text{NH}_3$ -treated: a sample which had previously been treated with hydrochloric acid was stirred for 30 mins. at room temperature with 50–100 vols. of  $\text{N-NH}_3$ , centrifuged, and washed with several changes of 10% ammonium acetate on the centrifuge.

" $\text{SnCl}_2$ -treated": the adsorbent was refluxed for 30–60 mins. with 50–100 vols. of 10% solution of stannous chloride in concentrated hydrochloric acid. After cooling it was washed on the centrifuge first with concentrated acid, then several times with distilled water.

All adsorbents were dried at  $120^\circ$  for about 12 hours, ground to a fine powder and passed through a 150-mesh sieve. They were stored over anhydrous calcium chloride.

*Substrates.*—Vitamin-A solutions were prepared by dissolving the content of one "Adexolin" capsule (Glaxo Ltd.) in about 50 ml. of benzene. Dicinnamylideneacetone was prepared by the method of Baeyer and Villiger (*Ber.*, 1905, **38**, 582); it produced a deep violet colour. 4-Amino-2':3-azotoluene was a recrystallised commercial preparation; it produced a purple colour on acid clays. Benzidine was purified by conversion into the hydrochloride, recrystallisation from water, regeneration of the base, and recrystallisation from 95% ethanol.

Other substrates used for colour tests were:  $\beta$ -carotene (Roche Products Ltd.) (blue colour); 2-amino-4':5-azotoluene (green colour); *p*-dimethylaminoazobenzene (red colour); anisylideneacetone (red colour); dianisylideneacetone (purple colour); dibenzylideneacetone (yellow colour).

*Adsorption Isotherms.*—For each test four samples of adsorbents, weighing roughly 10, 30, 100, and 200 mg., were filled into tared 10-ml. ampoules, dried overnight at  $120^\circ$ , and weighed. Five ml. of a solution of the substrate in benzene, usually containing 0.5, 1.5, or 15 mg., were added. The ampoules were sealed and shaken at room temperature ( $18$ – $20^\circ$ ) for 4–5 hours. The concentration of the supernatant solution was then determined by the following methods: Aminoazotoluene was determined by direct colorimetry of the original benzene solution. Dicinnamylideneacetone: an aliquot of the benzene solution containing between 10 and 100 g. was evaporated to dryness in a vacuum and 10 ml

of a saturated solution of antimony trichloride in chloroform (dry and free from ethanol) were added. Determination by colorimetry followed. Benzidine: an aliquot of the benzene solution containing 10—100  $\mu\text{g}$ . was evaporated to dryness in a vacuum and taken up in 2 ml. of 0.2N-hydrochloric acid. After diazotisation and coupling with *N*-(1-naphthyl)ethylenediamine dihydrochloride according to Klein (*Ind. Eng. Chem. Anal.*, 1944, **16**, 536) a colorimetric estimation was carried out.

All absorption measurements were done photoelectrically with the aid of suitable filters after calibration curves had been established with standard solutions.

Our thanks are due to Dr. G. Nagelschmidt, English Clays Lovering Pochin Co. Ltd., for supplying some of the clay minerals used in this investigation.

UNIVERSITY OF DURHAM,  
KING'S COLLEGE, NEWCASTLE-ON-TYNE, 1.

[Received, February 14th, 1948.]

---