

## SURFACE ACIDITY OF MONTMORILLONITES

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**Abstract**—Surface acidity of almost homoionic montmorillonites was measured by titrating selected Hammett indicators adsorbed on the clay with *n*-butylamine.

As expected, the acidity is strongly affected by the exchangeable cations and the degree of hydration of the clay. Greater polarizing ability of the interlayer cations increases both the strength and number of acid sites per  $H_0$  value. The acidity of 'activated' or heated H-montmorillonite does not exceed that of untreated H-montmorillonite. The origin of the negative charge in the montmorillonite appears to affect the acidity of the clay.

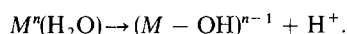
It is concluded that the very high acidities reported in the literature ( $H_0 < -5.6$ ) are apparent only and are due to physisorption of the indicator.

### INTRODUCTION

The ability of montmorillonite to donate protons (its 'surface acidity') causes the protonation of organic compounds such as amines (Yariv and Heller, 1970) and catalyzes many organic reactions, such as: the polymerization of styrene (Vallet *et al.*, 1972); the decomposition of the diazoacetate-ester (Delvaux *et al.*, 1964); the cracking and isomerization of hydrocarbons (Petrov, 1963) etc. A relationship has been established between the exchangeable cation and the ability of montmorillonite to donate protons to the adsorbed molecules (Russell *et al.*, 1968; Mortland and Raman, 1968). Walker (1967) reported that the presence of small and highly charged exchangeable cations in clays greatly enhances the decomposition of glycerol.

Touillaux *et al.* (1968), by applying pulsed magnetic resonance and conductivity measurements, found that the degree of dissociation of a water molecule adsorbed on montmorillonite is  $10^7$  times higher than in liquid water.

It seems, therefore, that the hydration water of the exchangeable cations is acidic, donating protons according to the scheme:



The acid strength of a solid surface (the surface acidity) is defined as its proton-donating ability, quantitatively expressed by the function  $H_0 = -\log a_{H^+} \gamma_{In}/\gamma_{InH^+}$  (Hammett and Deyrup, 1932), where  $a_{H^+}$  is the hydrogen ion activity of the surface acid and  $\gamma_{In}$  and  $\gamma_{InH^+}$  are activity coefficients of the basic and acid indicator forms, respectively. A complete description of surface acidity requires the determination of the acid strength of the sites and their number. The estimation

of acid strength of some clay minerals, including montmorillonite, on the basis of color changes of adsorbed Hammett indicators has been reported (Benesi, 1956, 1957; Hirschler *et al.*, 1961; Solomon *et al.*, 1971, 1972). These investigators found very strong sites by using dicinnamalacetone, benzalacetophenone and anthraquinone as indicators.

Drushell and Sommers (1966) concluded from a spectroscopic investigation of Hammett indicators adsorbed on various cracking catalysts "that all visible indicators for which the neutral species (base form) is colorless but has a strong absorption band just below  $400 \mu m$ , should be used with extreme caution, because a slight red shift produced by physisorption will result in a yellow color easily confused visibly with the true protonated species". This precaution applies particularly to benzalacetophenone and anthraquinone, both of which have been used in the past, without appropriate care, to determine the surface acidity of clays and other acid catalysts.

The present investigation deals with the effect of the exchangeable cation on the surface acidity of montmorillonite.

### EXPERIMENTAL

Four montmorillonites were examined: Wyoming (W) and Mississippi (M) montmorillonites and two samples, MF6 and MF14, from the 'black clay' bentonite deposit in Makhtesh-Ramon, Israel (Weissbrod, 1962).

Samples were saturated with sodium, magnesium, aluminum and hydrogen ions respectively, by the method previously described (Yariv *et al.*, 1968). Cs-W and Mg-Camp-Berteau (C.B.) montmorillonites were also prepared by the same method.

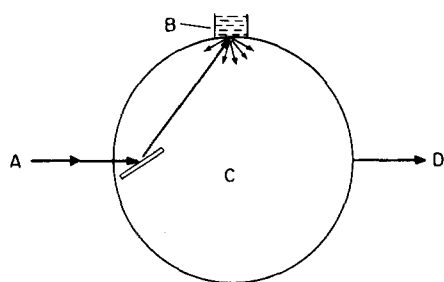


Fig. 1. Reflectance accessory: (A) incident light; (B) quartz tube with sample covered with *iso*-octane; (C) reflectance cell; (D) transmitted light.

All the samples were ground to pass a 100 mesh sieve and aliquots were dried at 130°C for 48 hr and stored over  $P_2O_5$ . In addition, aliquots of the *H*-samples were dried under ambient conditions and were cooled over  $P_2O_5$ . These were designated *H*(hot) and *H*(cold) respectively.

Part of each montmorillonite was 'activated' by refluxing 10% montmorillonite in 10% HCl solution at 90°C for 4.5 hr.

The Hammett indicators listed in Table 2 were of reagent grade quality. The *iso*-octane was of spectrophotometric grade.

#### Apparatus and procedure

The electronic spectra were recorded on a Cary Model 17 spectrophotometer. The reflectance spectra of the indicators adsorbed on the montmorillonites were obtained with a Cell Space Total Diffusion Reflectance Accessory, Cary Model 1411750 and 1511000.

Infra-red spectra of self supporting films of clays dried at 130°C for 48 hr were recorded on a Perkin-Elmer 237 grating instrument, X-ray diffraction patterns were obtained on a Seifert Iso-Debyeflex III A diffractometer, using a copper tube.

Absorption spectra of the indicator solutions were determined using a 1 cm quartz cell.

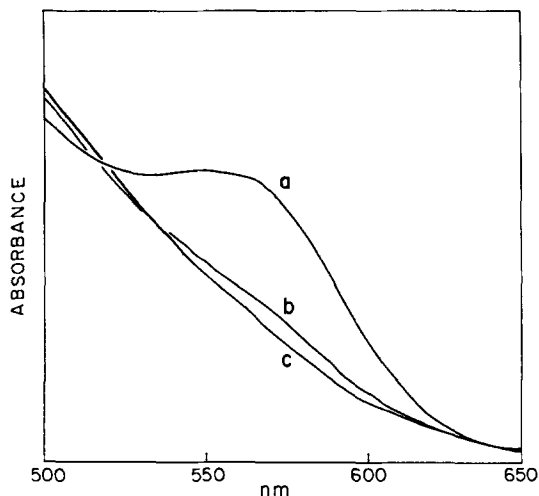


Fig. 2. Reflectance spectra of bromthymol blue adsorbed on Al-M (a), after addition of 0.01 m-equiv/g of *n*-butylamine (b) at the end-point, after addition of 0.02 m-equiv/g (c).

The titration procedure was as described by Drushel and Sommers (1966). Ten to twenty mg of the samples in *iso*-octane suspension were titrated with 0.005 N *n*-butylamine in *iso*-octane solution. Since the end-point of these titrations is not sharp it was checked by spectrophotometric titrations as follows: about 20 mg of the sample was weighed into a quartz tube, 1 cm<sup>3</sup> *iso*-octane and some drops of the indicator solution were added and the reflectance spectrum was recorded using the arrangement shown in Fig. 1. Small increments of titrant were repeatedly added to the stirred suspension. Each addition was followed by recording of the spectrum until the absorption due to the protonated indicator disappeared.

## RESULTS AND DISCUSSION

### Surface acidity measurements

A list of the indicators used, their colors in the neutral and protonated state and  $\lambda_{max}$  in the two forms are given in Table 1. Figure 2 shows an example of a spec-

Table 1. Some properties of the Hammett indicators used

Indicator	Color, $\lambda_{max}$ (cm <sup>-1</sup> )		pKa	H <sub>2</sub> SO <sub>4</sub> (%)*
	Acidic	Basic		
Bromcresol green	Yellow, 430	Green, 625	+4.6	
Benzene-azo-dimethylaniline	Red, 515	Orange, 395	+3.2	3.10 <sup>-4</sup>
Benzene-azo-diphenylamine	Purple, 540	Brownish-yellow, 380	+1.5	2.10 <sup>-2</sup>
Bromthymol blue	Red, 565	Brown, 420	-1.5	
Bromcresol green	Red, 580	Brown, 430	-3.7	
Benzalacetophenone†	Yellow, 440	Colorless, 310	-5.6	71
Anthraquinone†	Yellow, 410	Colorless	-8.2	91

\* Weight per cent of H<sub>2</sub>SO<sub>4</sub> in sulfuric acid solution which has the acid strength corresponding to the given pKa.

† These non-recommended indicators were not used.

trophotometric titration using bromthymol blue. Figure 3 and Table 2 show the measured surface acidity of the various montmorillonites. The strength of the acid sites is expressed by the Hammett acidity function  $H_0$ .

It can be seen that there is an excellent correlation between the exchangeable cations and the surface acidity of montmorillonite. The greater the polarizing ability of the cation, the more numerous and stronger the acid sites. A greater polarizing ability of the cation causes stronger polarization and dissociation of the water. Thus the acidity of montmorillonite decreases in the order:  $Al^{3+} > Mg^{2+} > Na^+$ .

Comparison of the surface acidity distribution of  $H$ (hot),  $H$ (cold) and activated montmorillonite with that of Al-montmorillonite (Fig. 3b and Table 2) shows that:

(a) The surface acidity of Al-montmorillonite is

nearly equal to that of  $H$ (hot)-montmorillonite. Since  $H$ -montmorillonite is rapidly transformed into Al-montmorillonite on heating, this result was to be expected.

(b) The surface acidity of  $H$ (cold)-montmorillonite is greater than that of any other sample. Two opposing factors operate: the hydrogen ion is obviously a source of strong surface acidity. However, to preserve the clay, at least partially, in the  $H$ -form, it cannot be dried at elevated temperatures and was therefore dried at ambient conditions only. Despite the higher water content, this sample was the most acidic.

The surface acidity is also affected by the nature of the montmorillonite itself. Yariv and Heller (1970) concluded from sorption of various amines, that C.B. montmorillonite has a greater tendency to donate protons than W-montmorillonite. Figure 3(d) expresses this conclusion quantitatively by comparing the acidities of

Table 2. Amount of acid sites equal to and stronger than the corresponding  $H_0$  value (m-equiv/g of sample)

$H_0$	-3.7	-1.5	1.5	3.2	4.6
Montmorillonite					
W.B.					
Natural		*	0.01	0.04	0.10
Na		*	0.02	0.05	
Mg	*	†	0.06	0.15	0.24
Al	†	0.02	0.14	0.25	0.38
$H$ (cold)	0.01	0.06	0.19	0.30	
$H$ (hot)	*	0.01	0.11	0.23	
Activated	†	0.02	0.13	0.20	
Cs			*	0.03	
Mis.					
Natural	*	†	0.03	0.08	0.18
Na	*	0.01	0.06	0.09	0.19
Mg	*	0.004	0.09	0.13	
Al	†	0.02	0.10	0.17	0.30
$H$ (cold)	0.005	0.05	0.21	0.31	
$H$ (hot)	*	0.004	0.10	0.18	
Activated	†	0.01	0.12	0.24	
MF6					
Natural	*	†	0.04	0.08	0.17
Na		*	0.02	0.05	0.14
Mg	†	0.01	0.06	0.17	0.30
Al	†	0.01	0.10	0.19	0.36
$H$ (cold)	†	0.04	0.15	0.27	
$H$ (hot)	†	0.02	0.08	0.20	
Activated	*	0.02	0.11	0.18	
MF14					
Natural	*	0.01	0.05	0.08	
Na		*	0.03	0.06	
Mg	*	0.02	0.05	0.11	0.22
Al	0.02	0.04	0.07	0.20	
$H$ (cold)	†	0.02	0.16	0.22	
$H$ (hot)	†	0.01	0.11	0.19	
Activated	*	0.01	0.12	0.15	

\* No acid sites equal to the given  $H_0$  value.

† Less than 0.005 m-equiv/g.

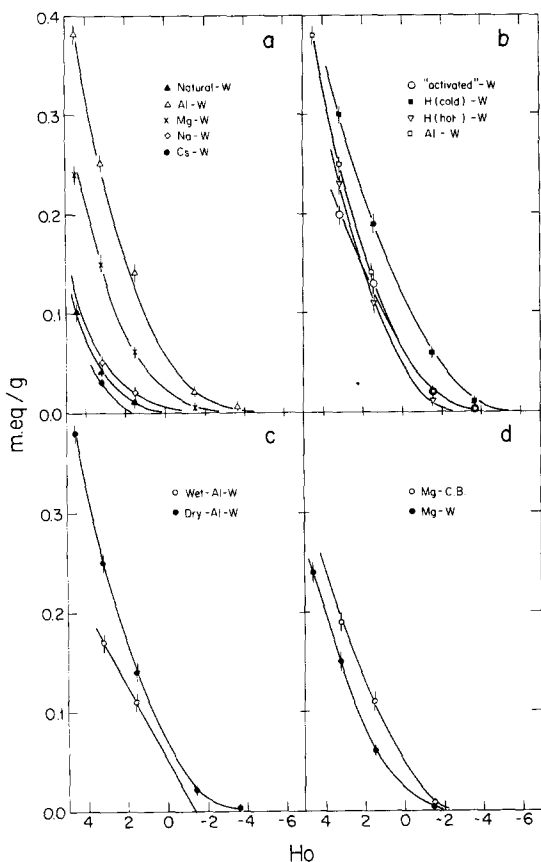


Fig. 3. Surface acidity distribution curves of various montmorillonites.

Mg-W and Mg-C.B. montmorillonites. In W-montmorillonites the negative charge derives approximately equally from the octahedral and tetrahedral layers whereas in C.B. it derives from the octahedral layer. A tetrahedral charge will cause a greater polarization of the hydration water but, on the other hand, will bind the proton more strongly to the tetrahedral layer. Proton donation will therefore be more readily effected in the C.B. than in the W-montmorillonite interlayers.

Hirschler *et al.* (1961), Mortland and Raman (1968), Solomon *et al.* (1971), Lahav (1972) and others found that the acidity of clay minerals increases as the mineral is dried. We compared the acidity of Al-W dried at 130°C with that of Al-W which was stored over water vapor at room temperature for 24 hr. The results (Fig. 3c) confirmed the conclusions reached by previous investigators.

By comparing our results with those given in the literature (Benesi, 1956, 1957; Hirschler *et al.*, 1961; Bailey *et al.*, 1968; Solomon *et al.*, 1971, 1972) it can be seen that there is disagreement in the region of the strongly acidic sites. While the literature reports acid

sites in montmorillonite corresponding to pKa values of  $-5.6$  and  $-8.2$  (i.e. equivalent to 71 and 91 per cent  $H_2SO_4$ , respectively, our results never reach such low pKa values. This contradiction is reconciled if we take into consideration that in all the previous studies the dicinnamalacetone, benzalacetophenone and anthraquinone indicators were used. By adding butylamine until the acidic color disappeared (i.e. until the physisorbed molecules were desorbed, instead of to the point of complete desorption of the protonated indicators, the authors obtained pKa values which were probably too low.

Additional confirmation of this argument is provided by the titration of benzalacetophenone adsorbed on Al-M-montmorillonite: 0.03 m-equiv/g acid sites stronger than pKa =  $-5.6$  were found, but less than 0.005 m-equiv/g stronger than pKa =  $-3.7$  and less than 0.02 m-equiv/g stronger than pKa =  $-1.5$ . It is, of course, impossible that there are more acid sites stronger than pKa =  $-5.6$  than sites stronger than pKa =  $-3.7$  or =  $-1.5$ . The acid strength distribution curves of montmorillonite in the literature (Benesi, 1957; Hirschler, 1961) are parallel to the abscissa over a wide range of pKa. This implies that only very weak and very strong acid sites occur, which *a priori* seems improbable. It has previously been proved wrong for cracking catalysts (Kevorkian *et al.*, 1963; Kubokawa, 1962), and in the present study also for montmorillonites.

#### Infra-red spectra

Figure 4 shows the 1500–1800  $cm^{-1}$  region of Cs-, Na-, Mg- and Al-W-montmorillonite. The absorption band at 1630  $cm^{-1}$  is attributed to the OH bending frequency of water molecules and absorption in the 1720  $cm^{-1}$  region to  $H_3O^+$  (Falk *et al.*, 1957).

It is apparent that the intensity of the  $\sim 1720$   $cm^{-1}$  band relative to that at  $\sim 1630$  decreases from Al- to Mg- to Na-montmorillonite, confirming that acidity decreases in this order.

The relatively strong 1720  $cm^{-1}$  band recorded with Cs-montmorillonite will be discussed below.

#### X-ray diffraction

Of the four montmorillonites used, W was the only one which did not become amorphous on activation. It is known that W-montmorillonite cannot be activated while M (Nutting, 1943) and Ramon bentonite (Fisher *et al.*, 1965) can.

The X-ray diffractometer traces (Fig. 5) show that *n*-butylamine penetrates between the layers of Na-, Mg- and Al-montmorillonite despite the low water content of the clays. The very small shift of the diffraction maximum with Cs-montmorillonite indicates that

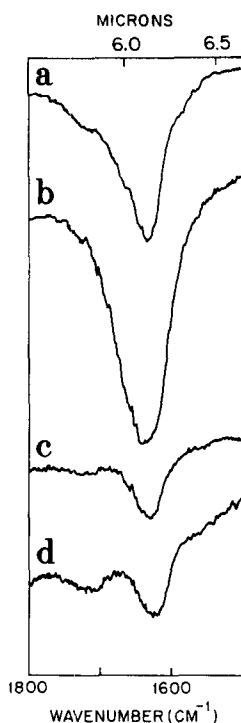


Fig. 4. Infra-red spectra of Al-W (a), Mg-W (b), Na-W (c), Cs-W (d).

only minor amounts of *n*-butylamine penetrate between the layers and that probably only a few layers are involved.

Whether the indicator itself penetrates between the layers or not is immaterial. Only after the butylamine has titrated all the acid sites stronger and equal to the *pK*<sub>a</sub> of the indicator, both outside and inside the layers, will the indicator be displaced from wherever it is sorbed.

It must be stressed that surface acidity, especially that of montmorillonite, is not an absolute value but is always measured relative to a reagent—here *n*-butylamine—and to the experimental conditions. If a correlation is sought between the measured surface acidity and an acid catalyzed reaction the reactant, like the butylamine, must penetrate between the mineral layers. It must also be established that there is no steric effect which will prevent the reactant from reaching some of the acid sites. According to Solomon *et al.* (1972), such steric effects do occur. Edge sites, though catalytically active, account for only a minor amount of the total acidity.

The significance of relative rather than absolute surface acidity is well illustrated by Cs-montmorillonite. Infra-red spectra show a high  $H_3O^+/H_2O$  ratio in the

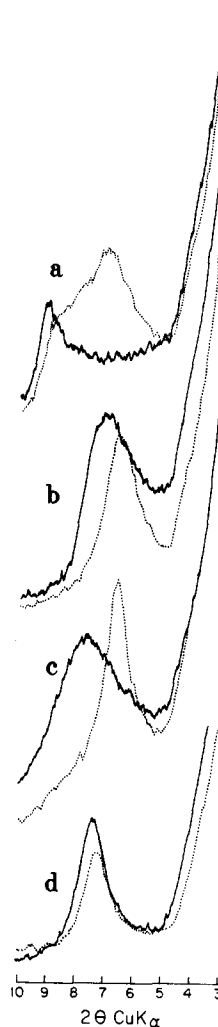


Fig. 5. X-ray diffractometer traces of Na-W (a), Mg-W (b), Al-W (c) and Cs-W (d) dried at 130°C for 48 hr (—), after addition of *n*-butylamine (.....).

interlayers. It appears that the few water molecules left on drying are strongly polarized by the Ca and Mg ions which remained non-exchanged when the montmorillonite was saturated with Cs. The  $d_{001}$ -spacing of the dried Cs-montmorillonite, about 11.55 Å, is essentially unchanged on treatment with butylamine. It seems that the amine does not penetrate between the layers although the montmorillonite is not collapsed (Fig. 5d). One explanation is that heating collapses the frayed edges and prevents penetration by the amine although the entire layers are not collapsed, as seen on the X-ray diffraction pattern. The acid sites measured are therefore on the outer surface only and few sites with relatively high  $H_0$  values are observed (Fig. 3a).

## CONCLUSION

The acid strength distribution curves of montmorillonite can be evaluated by careful use of Hammett indicators. The nature of the curves is largely determined by the exchangeable cations: the greater their polarizing ability, the greater the dissociation of the water of hydration, causing stronger and more numerous acid sites per  $H_0$  value. However, examination of a series of monoionic montmorillonites showed that the strong acidity ( $H_0 < -5.6$ ) claimed by previous investigators is not attained.

The acid strength of montmorillonite increases with decreasing amounts of interlayer water. It is also affected by the position of the negative charge of the clay: substitution in the octahedral sheet seems to cause stronger acidity than corresponding substitution in the tetrahedral sheet.

It should be emphasized that the acid strength determined by this method refers to a particular reagent, butylamine in the present study.

Using acid site distribution curves of this type, it seems possible that by a judicious choice of montmorillonite, interlayer cation and amount of water, a series of catalysts might be prepared having appropriate acid strength for specific acid catalyzed reactions. It may also prove possible to derive information about the seat of negative charge of clay minerals from such curves.

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**Résumé**—L'acidité de surface de montmorillonites pratiquement homoioniques a été mesurée en titrant par la *n* butylamine des indicateurs de Hammett sélectionnés, adsorbés sur l'argile.

Comme on peut s'y attendre, l'acidité est fortement affectée par les cations échangeables et le degré d'hydratation de l'argile.

Un pouvoir polarisant des cations interfeuilletés plus élevé augmente à la fois la force et le nombre des sites acides pour une valeur de  $H_0$ .

L'acidité de la montmorillonite-H "activée" ou chauffée ne dépasse pas celle de la montmorillonite-H non traitée. L'origine de la charge négative de la montmorillonite semble affecter l'acidité de l'argile.

On conclut que les très fortes acidités citées dans la littérature ( $H_0$  inférieur à  $-5,6$ ) sont seulement apparentes et sont dues à la physisorption de l'indicateur.

**Kurzreferat**—Die Oberflächenazidität von nahezu homoionischen Montmorilloniten wurde durch Titration von an dem Ton adsorbierten ausgewählten Hammet-Indikatoren mit *n*-Butylamin gemessen.

Wie erwartet, wird die Azidität stark durch die Art des austauschbaren Kations und den Hydratationsgrad des Tons beeinflusst. Größere Polarisierbarkeit der Zwischenschichtkationen erhöht sowohl die Stärke als auch die Anzahl der sauren Austauschplätze pro  $H_0$ -Wert. Die Azidität von 'aktiviertem' oder erhitztem H-Montmorillonit übersteigt nicht diejenige von unbehandeltem H-Montmorillonit. Die Herkunft der negativen Ladung im Montmorillonit scheint die Azidität des Tons zu beeinflussen.

Es wird geschlossen, daß die sehr hohen Aziditäten, über die in der Literatur berichtet wird ( $H_0 < -5,6$ ), nur scheinbaren Charakter haben und die Folge einer physikalischen Adsorption des Indikatoren sind.

**Резюме** — Поверхностная кислотность большей части гомоионных монтмориллонитов измерялась титрованием избранных указателей Хаммет адсорбированных на глине *n*-бутиламиноом. Как предполагалось, на кислотность сильно влияют обменные катионы и степень гидратации глины. С увеличением поляризационной способности катионов промежуточных слоев увеличиваются как кислотность так и количество кислых участков на величину числа  $H_0$ . Кислотность «активированных» или нагретых H-монтмориллонитов не превышает кислотности необработанных. Появление отрицательного заряда монтмориллонита повидимому влияет на кислотность глины. В заключении говорится, что очень высокие числа кислотности, указываемые в литературе ( $H_0 < -5,6$ ), являются только кажущимися и зависят от физической сорбции индикатора.