ACID-BASE INTERACTIONS AND THE PROPERTIES OF KAOLINITE IN NON-AOUEOUS MEDIA

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Abstract—In non-aqueous systems, kaolinite can show, in addition to the physical interactions, considerable chemical activity. This study considers the chemical reactions that can occur at the kaolinite surface and explains these reactions in terms of acid-base interactions. In certain applications the chemical activity must be controlled if satisfactory products are to be obtained; for example, when kaolinite is used as a filler in rubber or as a diluent for insecticide powders. The concept of acid-base interactions is used to explain rheological and film properties in kaolinite-organic systems. The strength of the surface acid sites of kaolinite varies with the moisture content. At 1% moisture the surface is equivalent to 48% sulphuric acid whereas at 0% it is equivalent to 90% sulphuric acid. Therefore, the moisture level is extremely important and dry kaolinite will promote or catalyze many chemical reactions and where acid-base interactions are involved the presence of even small amounts of water usually retards or inhibits the reaction. Several examples explaining these interactions are given in the paper.

INTRODUCTION

THERE ARE numerous studies on the properties of kaolinite in aqueous systems and much of this work has been stimulated by the commercial use of kaolinite as a pigment in paper coatings, as an extender in latex paints, and as a ceramic raw material. In these aqueous systems kaolinite is generally regarded as a chemically inert entity and the properties contributed by the kaolinite to the system are usually explained in terms of the physical interactions that occur.

However, in non-aqueous systems, kaolinite can show, in addition to the physical interactions, considerable chemical activity which contrasts with, and is not readily predicted by, its behavior in the presence of water. In fact the chemical activity is of such magnitude that it is the basis for selecting kaolinite as a base for catalyst preparations and as a component of pressure sensitive copying paper (Green, 1952). In other applications, for example when used as a filler or extender in rubber (Solomon and Swift, 1967) or as a diluent for insecticide powders (Benesi et al., 1959) the chemical activity must be controlled if satisfactory products are to be obtained.

In this paper we propose to discuss the signifi-

cance of acid-base interactions to the chemistry of kaolinite in non-aqueous systems and then to indicate how these interactions can affect the rheology of kaolinite dispersions and the properties of filled composites in which kaolinite is the major pigment or filler.

EXPERIMENTAL AND RESULTS

Measurement of acidity

All solvents and amines were AR quality which were further purified and thoroughly dried by standard methods. The indicators used were those described by Benesi (1957) and were recrystallized to have melting points corresponding to those reported in the literature. The titration procedure was similar to that used by Benesi (1957) except that the sample (1.000 g undried) was placed in small screwcap bottles and then heated at 110°C for 2 hr. The bottles were then removed from the oven, immediately capped, and placed in a desiccator until cooled to room temperature. After addition of a solution of the amine in benzene and equilibration for 1 hr (longer times of equilibration made no difference to the results), the samples were tested with indicators. The number and maximum acidity of the acid sites is shown in Table 1.

Mineral	pK_a range of strongest sites	Total acidity to $pK_a 4.0$ (meq amine/g mineral)
Kaolin	< -8.2	0.04
Montmorillonite	-5.6 to -8.2	> 0.2
Attapulgite	< -8.2	> 0.2
Talc	4·0 to 3·3	0.005
TiO ₂ -silica-alumina		
coated	3·3 to 2·8	0.005
Calgonized kaolin	1.5 to - 3.0	0.04
Sodium kaolin	-3.0 to -5.6	0.03
Alumino-silicate		
catalyst	< -8.2	0.20

Table 1. The number and maximum acidity of acid sites on dry minerals

Polymerization of styrenes on kaolinite

One g kaolinite was added to 10 ml styrene or substituted styrenes. After 30 min the polymer was precipitated by addition to methanol. The polymer was then filtered off, dried and weighed. The results using kaolinite containing various amounts of water are shown in Table 2.

Decomposition of peroxides and hydroperoxides. Cumene hydroperoxide, CHP (approx. 70%) was treated as follows: to 10 ml of CHP was added cold aqueous sodium hydroxide solution (30 ml 25%) and the mixture allowed to stand for 2 hr. The precipitate which formed was filtered off, washed with sodium hydroxide solution and then with a little acetone. The precipitate was dissolved in water (100 ml) and this solution was neutralized with hydrochloric acid, acidified with carbon dioxide and extracted with petroleum ether $(3 \times 30 \text{ ml of b.p. } 30\text{--}40^{\circ}\text{C} \text{ aromatic free})$. To remove any acid present the petrol extract was washed with bicarbonate solution. After drying the extract overnight (anhydrous Na₂CO₃) it was distilled under reduced pressure and an inert atmosphere and gave cumene hydroperoxide b.p. 61-63°C at 0.1 mm. The purity estimated by iodometric titration was 99.8%.

Dicumyl peroxide (DCP) (99% by iodometric titration) was used without further purification.

The kaolinite used was Hydrite 10-a commer-

cial grade, supplied by Georgia Kaolin Company, with a particle size of approximately 0.55μ and a water content as received of 0.6% when measured by drying for 2 hr at 110° C.

Kinetic studies. Two techniques were used to follow the kinetics of the clay initiator reactions. In method A which was used where the ratio of clay to initiator and solvent is small, the clay, initiator and solvent were stirred under a nitrogen atmosphere in a 250 ml flask thermostated at 30°C. Samples were withdrawn at intervals and the residual peroxide or hydroperoxide measured by iodometric titration. In method B, used for higher clay loadings, the clay, initiator and solvent were weighed into ampoules. These were tumbled in a water-bath and the reaction followed as in method A. The results are shown in Table 3.

Table 3. The effect of moisture content of kaolinite (Hydrite 10) on the rate of breakdown of cumene hydroperoxide and dicumylperoxide

% Moisture	% CHP remaining after 2 hr	% DCP remaining after 2 hr
0.6	1	45
1.5	9	71
3	97	87
6	99	- 90

Table 2. The effect of moisture content of kaolinite on the polymerization of styrenes

Moisture content of kaolinite	Styrene (%)	Yield of polymer p-methylstyrene (%)	p-Methoxystyrene (%)
Dry clay	100	100	100
0.2%	0	100	100
0.6%	0	0	100

The effect of organic bases on the neutralization of kaolinite

Titration of the kaolin with solutions of methanol, ethanol and *n*-butanol in benzene was carried out in a similar manner. The effect of water was determined by saturating the clay with water and then partially drying the clay.

Acetone, methyl ethyl ketone, dioxane, and ethyl acetate in benzene were also added to dry kaolin. The pK_a of the kaolin solvent system was measured in each case. The neutralizing effect of these bases was in the order water, methanol, ethanol, n-butanol, acetone, methyl ethyl ketone, ethyl acetate, and dioxane.

Rheology measurements

Twenty grams kaolinite was dispersed in 80 g medicinal paraffin oil using a high speed blender. The viscosity of this dispersion was measured on a Haake Rotovisco using concentric cylinder measuring systems. The Yield Stress was calculated using Casson's equation:

$$au^{1/2} = au_0^{1/2} + \eta_\infty^{1/2} D^{1/2}$$

where

 $\tau = \text{shear stress (dyne cm}^{-2})$ $\tau_0 = \text{yield stress (dyne cm}^{-2})$

 $D = \text{shear rate (sec}^{-1})$

 η_{∞} = viscosity at infinite shear rate (poise).

The yield stress of kaolinite with various additives is shown in Table 4. For linseed oil, 30 g of kaolinite was dispersed in 70 g linseed oil. The viscosities were measured on a Brookfield Viscometer. The results are shown in Table 5.

Forty grams kaolinite was dispersed in 60 g 51.4% alkyd resin in white spirit. The viscosities were measured on a Brookfield Viscometer and the results are shown in Table 6.

Measurement of properties of kaolinite filled rubber

Kaolinite and polyphosphate treated kaolinite, (Solomon and Swift, 1967), were processed into

Table 4. The effect of basic additives on the yield stress of 20% kaolinite dispersion in paraffin oil

Additive*	Yield stress (dyne cm ⁻²)
1/2% Water	> 1800
No additive	480
1% Methyl nonyl ketone	540
1% n-Undecanol	200
1% n-Decylamine	73

^{*}The clay was dried at 105° for 2 hr before use. The percent additive is based on the weight of dry clay.

Table 5. The viscosity of 40% kaolinite dispersions in linseed oil

Kaolinite	Viscosity (Brookfield 30 rpm) (poise)
Undried Hydrite 10	> 200
Dried Hydrite 10	43
Kaophobe 5	36

Table 6. The effect of moisture on the viscosity of 40% Hydrite 10 dispersions in alkyd solution*

Hydrite 10	Viscosity† (poise)		
Dried	465		
Undried	278		

^{*51.4%} solution of alkyd in white spirit.

a rubber mix using the following formula: SBR 1502, 500 parts (by weight); sulfur, 15 parts; cyclohexyl benzothionyl sulfide, 10 parts; zinc oxide, 25 parts; coumarone resin, 37.5 parts; clay, 260 parts. The rubber mixes when cured gave the results shown in Table 7.

Table 7. Influence of "acid" kaolin on vulcanization of rubber

Filler		Ultimate tensile strength	Elongation at break	Mod	lulus si	
present	Cure	(psi)	(%)	300%	500%	Hardness
Kaolin*	10 min at 160°C	1640	810	200	350	53
Polyphosphate modified kaolin†	10 min at 160°C	2640	700	380	930	61

^{*}Hydrite 10.

[†]Measured at 21°C at 12 rpm using spindle 4 on a Brookfield viscometer.

[†]Hydrite 10S.

		l stress e cm ⁻²)	Gel time	
Clay	Dried	Undried	Dried	Undried
Amino treated		<u></u> ,		
Hydrite 10	_	_	_ '	35 min
Hydrite 10	170	45	> 500 min	> 500 min
Hydrite 10S	17		> 500 min	70 min
Unfilled resin	No yie	ld stress	60 n	nin

Table 8. Properties of kaolin/polyester mixtures

Kaolinite filled unsaturated polyesters

Forty grams kaolinite or treated kaolinite was dispersed in an unsaturated polyester resin (R 9516, manufactured by Monsanto Australia Ltd.). The viscosities of the dispersions were then measured on a Haake Rotovisco and are shown in Table 8.

To these polyester clay dispersions was added cobalt naphthenate (equivalent to 0.06% cobalt metal per 100 g polyester resin) and methyl ethyl ketone peroxide (2.0 parts per 100 g polyester resin). The gel times shown in Table 8 were measured on a Cambridge-Techne automatic gel timer.

DISCUSSION

It is convenient to first consider the properties of kaolinite in the presence of relatively simple organic compounds and then to extend the discussion to the more complex systems where polymeric organic material is present.

The chemical activity of kaolinite

The chemical activity shown by kaolinite in non-aqueous media is best explained by attributing to the kaolinite the characteristics of an acid. Here the term acid is used in a very general sense to include Bronsted acidity (ability to donate a proton), Lewis acidity (ability to accept an electron pair), and the capacity to act as an oxidant (accept one or more electrons).

The majority of naturally occurring or beneficiated kaolinites used in organic media are supplied at a specified moisture content of less than 1% (Georgia Kaolin Co.). Here the moisture content is defined as the weight loss on drying at 110°C. The surface moisture could be expected to reach values close to 0% during the processing of the clay into many organic systems where elevated temperatures are used and hence our interest should center around the acidity of the clay with a surface moisture in the range of 0-1%. It is indeed unfortunate that the acidity of clays under these conditions is rarely mentioned by the suppliers. The acidity figures given are usually measured at 20% solids in water (Georgia Kaolin

Co.) and under these conditions most kaolinites give a pH of between 4.5 and 7.

The surface acidity of "dry" kaolinite can be measured by Hammett indicators which are organic bases of various basicities. The number of acid sites can be measured by a titration procedure usually involving butylamine (Benesi, 1957).

Figure 1 shows the strength of the surface acid sites of kaolinite at various moisture contents. Three points of special significance to the present discussion are:

- (1) The extremely acidic surface of dry kaolinite which at 0% moisture is equivalent in acidity to a solution of 90% sulphuric acid.
- (2) Over the 0-1% range of moisture contents there is a tremendous change in the strength of the acid sites; at 1% moisture the surface is equivalent to 48% sulphuric acid whereas at 0% it is equivalent to 90% sulphuric acid.
- (3) This wide acidity range occurs over the normal spectrum of conditions encountered in the commercial use of kaolinite.

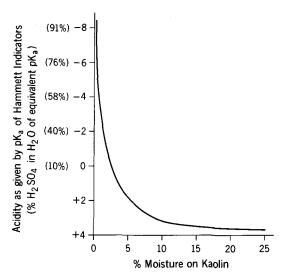


Fig. 1. The effect of moisture on the maximum surface acidity of kaolinite.

The number of acid sites as measured by butylamine titration is shown in Table 1 where the acidity of kaolinite is compared with that of other minerals. Of interest is the comparison between a silica-alumina cracking catalyst and kaolinite. The kaolinite has sites as strong as those on the cracking catalyst but there are only about 1/5 as many.

Dry kaolinite will promote or catalyze many chemical reactions and where acid-base interactions are involved the presence of even small amounts of water usually retards or inhibits the reaction. In effect, the water functions as a base and neutralizes preferentially the strongest acid sites (in some instances adsorption processes will also be affected). For example, (Table 2), styrene, p-methylstyrene, and p-methoxystyrene all undergo a vigorous exothermic polymerization on dry kaolinite. If the kaolinite contains 0.2% water only the p-methylstyrene and the p-methoxystyrene polymerize, and if the clay contains 0.6% water only the p-methoxystyrene polymerizes (Solomon and Swift (unpublished data)). These results are to be expected because the order of susceptibility to acid catalyzed polymerization is p-methoxystyrene > p-methylstyrene > styrene. A further example of the effect of water on the kaolinite acidity comes from studies on the rate of breakdown of organic peroxides and hydroperoxides (Solomon et al., 1971). From the results in Table 3 it can be seen that once again the driest clay is the most active and gives the fastest rate of breakdown. Similar results are found in the reactions of leuco dyes, such as malachite green, with kaolinite (Solomon, Loft and Swift, 1968).

Bases other than water can also neutralize the kaolinite surface (Solomon, Swift and Murphy, 1971) and a knowledge of the relative effectiveness of the various organic bases is vital for the successful industrial use of kaolinite. Water and short chain alcohols (methanol, ethanol) are much less effective than amines in neutralizing the surface. For example, on an equivalent basis ethanol is only a tenth as effective as ethylamine in neutralizing to a p K_a of -5.6. Alcohols above C_3 are even less effective and this is consistent with the lower basicity shown by the longer chain alcohols. The results also indicate that ketones are only weak bases and ethers and esters very weak bases. Thus we can conclude that, in general, the order of decreasing basicity in the neutralization of kaolinite is: amines $> C-C_2$ alcohols, water > ketones $> C_3$ and above alcohols, esters, ethers > hydrocarbons.

The rheology of kaolinite dispersions

It has been shown above that dry kaolinite interacts with simple organic bases and we would therefore expect that similar interactions would occur with high molecular weight organic molecules which contain basic substituent groups. These interactions should have a great influence on the rheology of kaolinite dispersions in oils or polymers.

In paraffin oil the presence of surface moisture on the kaolinite results in a significant increase in the yield stress and viscosity of a dispersion (Loft and Solomon, 1972a) (Table 4) as a consequence of a number of effects. A more clear cut illustration of the effect of acid-base interactions on flow properties is given by comparison of the effect of additives of the same chain length on the paraffin oil/dry kaolinite system. It is found that the decrease in yield stress and viscosity of a suspension is proportional to the basicity of the functional group of the additive used (Table 4). The effect of the acid-base interaction in these systems is to convert the kaolinite surface to a paraffin-like surface, thus increasing the compatibility of the kaolinite with the oil and decreasing the tendency for flocculation. Again, amine has the greatest effect.

If linseed oil (a glyceride ester) is used as the medium (Loft and Solomon, 1972b) the interaction between the medium and the clay is stronger than is found with paraffin oil (Table 5). This is to be expected because linseed oil is a stronger base. Because of this interaction, the dry clay in linseed oil behaves almost identically to a commercial kaolin which has a coating of oleyl radicals on the surface. In other words, the dry clay/linseed oil mixture forms in situ an organophilic clay.

With linseed oil and paraffin oil (high molecular weight monomeric materials), interactions between the medium and kaolinite are likely to result in dispersion and reduced viscosity rather than flocculation. With polymeric media however, the possibility of flocculation by interaction of a single polymer chain with a number of clay particles exists. Hence, it is of interest to examine the effect of surface moisture on acid-base interactions between kaolinite and a polymer which contains basic groups.

In an alkyd resin the basic groups present are hydroxyls and esters. These groups interact with the dry surface, leading to particle-particle bridging (as shown by the high viscosity, 465 poise, for a 40% w/w dried Hydrite 10 dispersion in alkyd) (Table 6). On the other hand, the less acidic moist surface has less interaction and the dispersion viscosity is almost halved, 278 poise, for 40% undried Hydrite 10 compared with 465 poise for 40% dried Hydrite 10 dispersion in alkyd. This also confirms that water is a stronger base than long chain alcohols or esters which do not displace the

water from the kaolinite acid sites despite their higher concentration in this system (Fig. 2).

Thus the concept of acid-base interaction can be used to explain at least partially, the rheological behavior of clay in non-aqueous media.

VEHICLE.	DRIED KAOLIN	UNDRIED KAOLIN
Linseed oil (nonpolymeric ester)	organophilic particle Low Viscosity	water bridging High Viscosity
Alkyd polymeric base —OH,—COOH—COOR	(clay) (clay) Higher Viscosity	COOH OH Clay Clay water bridging High Viscosity

Fig. 2. Schematic representation of acid-base interactions in kaolin dispersions.

The properties of kaolinite/polymer composites

Most polymers are used industrially as complex mixtures which contain a variety of pigments, fillers and additives. To illustrate the significance of acid-base interactions to the properties of these composites it is desirable to examine model systems in which kaolinite is the only pigment or filler.

Comparison of paint compositions (Solomon and O'Leary, unpublished data) prepared from a 50% oil length alkyd resin, driers, and kaolinite showed that the dry clay gave a formulation which dried to a harder film than the undried clay. The film from the dry kaolinite formulation showed no water absorption during 24 hr total immersion, whereas the film from the undried kaolinite showed a 25% weight increase. At this stage of our experiments we suggest that these results be taken as an indication that differences are possible between formulations based on dry and undried kaolinite. A detailed explanation for the reasons for the difference is difficult because of the many contributing factors to the drying process.

Other examples of the effect of the surface moisture of kaolinite on polymer properties can readily be found. For example, in rubber composites (Solomon and Swift, unpublished data) where the interactions would be expected to be similar to those previously noted in paraffin oil, it is usual practice to add small quantities of amines to obtain a better cure. The amines neutralize the surface and prevent premature breakdown of the vulcanizing agents (e.g. peroxides and hydroperoxides). A similar result (Solomon and Swift, unpublished data) can be obtained using a long chain polyphosphate to neutralize the kaolin surface (Table 7).

In kaolin filled unsaturated polyesters, dry clay may cause rapid polymerization of the styrene giving negligible pot life, or destroy the initiator. Undried or neutralized kaolin (polyphosphate or amine treated) should be used in these polyesters. The very much shorter gel time given by the less acidic kaolins is apparent from the results in Table 8.

CONCLUSIONS

Acid-base interactions contribute significantly to the properties of kaolinite in non-aqueous kaolinite dispersions. The interactions have a bearing on the chemistry, on the rheology and on the final properties of non-aqueous kaolinite systems.

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Résumé – Dans les systèmes non aqueux, la kaolinite peut montrer, en plus des interactions physiques, une activité chimique considérable. Ce travail se rapporte aux réactions chimiques qui peuvent se produire à la surface de la kaolinite, et explique ces réactions en termes d'interactions acide-base. Dans certaines applications, l'activité chimique doit être contrôlée si l'on désire obtenir des produits satisfaisants; c'est le cas par exemple, lorsque la kaolinite est utilisée comme charge minérale dans

le caoutchouc ou comme diluant dans les poudres insecticides. Le concept d'interactions acide-base est utilisé pour expliquer les propriétés rhéologiques et de films dans les systèmes kaolinite-produit organique. La force des sites acides de surface de la kaolinite varie avec la teneur en eau. A une humidité de 1% la surface est équivalente à de l'acide sulfurique à 48%, alors qu'à 0% d'eau, elle est équivalente à da l'acide sulfurique à 90%. Ainsi, le taux d'humidité est extrêmement important et de la kaolinite sèche facilitera ou catalysera de nombreuses réactions chimiques; lorsque des interactions acide-base sont en cause, la présence d'eau, même en quantité très faible, retarde ou inhibe en général la réaction. Plusieurs exemples expliquant ces interactions sont donnés dans cet article.

Kurzreferat – In nicht-wässrigen Systemen kann Kaolinit, zusätzlich zu den physikalischen Wechselwirkungen, beträchtliche chemische Aktivität aufweisen. In dieser Arbeit werden die chemischen Reaktionen betrachtet, die an der Oberfläche des Kaolinits stattfinden können, und diese Reaktionen durch Säure-Base Wechselwirkungen erklärt. In gewissen Anwendungsgebieten muss die chemische Aktivität gesteuert werden wenn befriedigende Produkte erhalten werden sollen, zum Beispiel, wenn Kaolinit als Füllmaterial in Gummi oder als Verdünnungsmittel für insektentötende Pulver verwendet wird. Der Begriff der Säure-Base Wechselwirkungen wird verwendet um die rheologischen und Filmeigenschaften in kaolinitorganischen Systemen zu erklären. Die Stärke der Säurestellen an der Oberfläche von Kaolinit variiert mit dem Feuchtigkeitsgehalt. Bei 1% Feuchtigkeit entspricht die Oberfläche 48% Schwefelsäure während sie bei 0% einer Stärke von 90% Schwefelsäure entspricht. Das Feuchtigkeitsniveau ist daher äusserst wichtig und wenn en sich un Säure-Base Wechselwirkungen handelt kann die Gegenwart auch kleinster Mengen von Wasser die Reaktion verlangsamen oder sogar verhindern. In diesem Artikel werden verschiedene Beispiele angeführt, die diese Wechselwirkungen veranschaulichen.

Резюме — В безводных системах каолинит проявляет, кроме физических взаимодействий, значительную химическую активность. Настоящая работа рассматривает происходящие на поверхности каолинита химические реакции и объясняет их в терминах взаимодействия кислот и оснований. Если требуется получить для некоторых применений удовлетворительные продукты, то химическую активность надо контролировать; например, когда каолинит используется в качестве наполнителя для резины или как растворитель для порошкообразных инсектицидов. Принцип взаимодействия кислот/оснований применяется для объяснения реологических и пленочных свойств каолинитных органических систем. Прочность кислотных сторон поверхности каолинита изменяется с изменением влагосодержания. При 1% влажности поверхность эквивалентна 48%—ной серной кислоте, а при 0% эквивалентна 90%—ной серной кислоте. Поэтому, уровень влажности чрезвычайно важен и сухой каолинит может быть катализатором многих химических реакций и ускорять их, а где происходит взаимодействия кислот-оснований, присутствие даже малых количеств воды обычно замедляет или тормозит реакцию. В статье приводятся несколько примеров, объясняющих эти взаимодействия.