

VISCOSIMETRIC CONSTANTS OF SUSPENSIONS OF CLAY-POLYMER COMPLEXES

by

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ABSTRACT

The viscosimetric constants of aqueous suspensions of certain homoionic forms of montmorillonite and attapulgite were measured following adsorption of different kinds and quantities of organic polymers. Dissymmetry and interaction of the clay-organic complexes were then calculated from the Schulz-Blaschke equation and their structures deduced.

A positive, linear relationship was found between the dissymmetry of H- and Al-montmorillonite, respectively, and the amount of vinyl acetate maleic anhydride (VAMA) adsorbed. H-montmorillonite displayed the greater dissymmetry and it is inferred that H-montmorillonite complexes consist of an edge-to-edge linkage of clay particles through lattice-aluminum-carboxyl bonds. Al-montmorillonite permits three kinds of linkage: edge-to-edge (as with H-montmorillonite), external flat surface-to-surface (producing a "stacked" structure), and surface-to-edge, the last two involving exchangeable aluminum-carboxyl bonds. Edge-to-edge linkages probably predominate.

Ca-montmorillonite is unaffected by less than 8 parts of VAMA per thousand of clay. Edge-to-edge linked clay particles appear at this ratio and interaction diminishes. Delayed structural organization can be explained by low polymer adsorption at high initial pH. Maximum dissymmetry of H-montmorillonite-VAMA complexes occurred after titration with NaOH to pH between 6 and 8, above which mutual repulsion between highly dissociated polymer and clay may restrict linkage.

H-attapulgite-VAMA complexes are dissymmetrical for low VAMA adsorption but increased adsorption reduces dissymmetry and bundles of edge-to-edge linked particles are formed.

Probable structures of montmorillonite complexes with other polymers are also discussed.

INTRODUCTION

The physical and chemical behavior of soil material is greatly affected by the spatial arrangement of the constituent particles. Apart from strictly mechanical forces, the clay and its adsorbed substances, particularly the

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adsorbed organic compounds, probably exert the greatest direct influence upon particle arrangement, although little is known of the controlling mechanisms. In order to obtain a greater understanding of the latter the authors have measured the viscosities of suspensions of different clays upon which different ions and organic polymers had been adsorbed. Estimates of the shape and interactions of these clay-organic complexes were then made from the calculated viscosimetric constants. The results, with discussion and conclusions, constitute the present article.

Simha (1948) pointed out that various investigators have found close agreement between the viscosimetric, sedimentation and diffusion, and electron microscope and X-ray methods for evaluating the shape of small particles. Earlier he had related the intrinsic viscosity to a function of the axial ratios of nonspherical particles, the relation being such that a high intrinsic viscosity implies a large axial ratio and is thus an expression of particle shape (Simha, 1940). When referred to clay particles the axial ratio is also called the dissymmetry and, as used by Packter (1956a, 1956b, 1957), Granquist (1959), and Kahn (1959), is the ratio of their average surface diameter to the platelet lattice thickness. Elongated particles and thin, flat particles are thus highly dissymmetrical and have a correspondingly high intrinsic viscosity whereas particles or aggregates having a more compact form have lower dissymmetry.

Packter (1957) examined the structure of numerous complexes of montmorillonite-carboxymethylcellulose by viscosimetric means and contributed significantly to this method. His work in large part stimulated these studies; so, too, did the work of Granquist (1959). The many earlier studies of the rheology of drilling muds were concerned chiefly with yield points and thixotropy rather than with aggregate morphology of clay-organic complexes (Broughton and Hand, 1938; Norton, Johnson and Lawrence, 1944; Langston and Pask, 1958; Schulz, 1957). The well known, critical work of Scott-Blair (Scott-Blair and Crowther, 1929; Scott-Blair, 1930) with soil clays was similarly directed.

The viscosity of a dilute suspension during Newtonian flow is greater than that of the suspending liquid owing to the distortion of the flow pattern by the suspended particles whose shape and orientation affect this pattern and hence the viscosity. If electrically charged, the orientation, interaction and hydrodynamics of the particles will be affected and, in turn, the viscosity of the suspension. Many viscosity equations have been proposed in order to allow for the particle-particle interaction and particle shape. They have been reviewed by Granquist (1959) and van der Watt (1960) who discussed and emphasized several advantages of the Schulz-Blaschke (1941) equation

$$\frac{\eta_{sp}}{c} = k [\eta] \eta_{sp} + [\eta], \quad (1)$$

in which η_{sp} is the specific viscosity ($\eta_{sp} = \text{relative viscosity} - 1$); η_{sp}/c is the viscosity number, or the specific viscosity divided by concentration of suspended material; $[\eta]$ is the intrinsic viscosity, or the viscosity number at infinite dilution ($[\eta] = (\eta_{sp}/c)_{c \rightarrow 0}$) and the coefficient, k , is considered to be a measure of the amount of particle-particle interaction. It is called the interaction index and is dimensionless. The specific viscosity also is dimensionless. If the concentration, c , of suspended particles has the dimensions ML^{-3} then the viscosity number and the intrinsic viscosity both have the dimensions $M^{-1}L^3$. Both hydrodynamic and electric interactions are believed to contribute to k although the exact contribution of either one alone cannot be determined.

Equation (1) was developed from and expresses the discovery of its authors that, for Newtonian liquids, there is a straight-line relationship between viscosity number and specific viscosity and that—for a number of molecular weight fractions of the methyl ester of polymethacrylic acid—the slopes of the straight lines were proportional to the intercepts on the viscosity number axis.

Since the viscosity and specific viscosity change with concentration it is sometimes useful to determine the specific viscosity at some arbitrarily chosen concentration. In this event eq. (1) may be rewritten

$$\eta_{sp} = \frac{[\eta]}{1/c - m}, \quad (2)$$

wherein $m = k[\eta]$ the slope of the straight line represented by (1). For a 1 percent suspension $c = 0.01$ g/ml and

$$\eta'_{sp} = \frac{[\eta]}{100 - m}. \quad (3)$$

The specific viscosity of a 1 percent suspension, η'_{sp} , thus may easily be calculated from the graphical measurements of $[\eta]$ and of m in a plot of viscosity number against specific viscosity, η_{sp} .

Equations (1) and (2) are based on assumed Newtonian behavior of the suspensions, and it is necessary when using (2) to choose a concentration such that $1/c > m$.

The most complete use of viscosity data is possible, however, only when the specific viscosity is measured in relation to concentration of suspended material, thus allowing determination of both intrinsic viscosity and interaction index. These values are constants for a clay suspension of definite chemical properties. They determine the viscosity of a Newtonian suspension of given concentration and temperature and may therefore be referred to as the *basic viscosimetric constants*.

MATERIALS AND METHODS

Clays and Polymers

Several clays and polymers were used, but the interactions of only two clays and three polymers concern us in the present work¹. The clays are montmorillonite (Mtm) from Belle Fourche, South Dakota, and attapulgite (Attp) from Attapulgus, Georgia. The polymers are vinyl acetate-maleic anhydride (VAMA) and two copolymers of methyl vinyl ether and maleic anhydride (PVM/MA Half Amide-5 and PVM/MA Half Amide-30). Some properties of the clay are given in Table 1.

TABLE 1.—CATION EXCHANGE CAPACITY, DENSITY AND PARTICLE SIZE DISTRIBUTION OF MONTMORILLONITE AND ATTAPULGITE

Clay	Cation Exchange Capacity (meq/100 g)	Density (g/ml)	Particle Size Distribution (μ , percent)					
			2-1.5	1.5-1.25	1.25-1.0	1.0-0.75	0.75-0.5	0.5-0
Montmorillonite	94.4	2.753	0.18	0.59	3.35	0.77	0.70	94.9
Attapulgite	42.4	2.644	1.83	0.08	5.34	0.11	96.5	

Viscosimeter

Viscosity measurements were made with a varying head capillary viscosimeter modeled after the instrument developed by Maron, Krieger and Sisko (1954). Our instrument differed from theirs in that its construction allowed both side-arm and flow capillary to be contained in the constant temperature water jacket which could be controlled to within 0.05 °C at any temperature between room temperature and 80 °C. All measurements were made at 30 °C. The viscosity equation derived by Maron, Krieger and Sisko (1954) for use with this type of viscosimeter is

$$\frac{d(\log_{10} h)}{dt} = - \left[\frac{M R^4 \alpha'_w}{8 \eta L r_w^2} \right] = - \frac{B_w}{\eta}, \tag{3}$$

wherein h = height of liquid in side-arm, r_w = radius of side-arm tube, above equilibrium height, η = viscosity,
 t = time, α'_w = an instrumental constant which includes the densities
 $M = \log_{10} e$, of water and mercury,
 R = radius of capillary tube,
 L = length of capillary tube, B_w = a constant.

¹ The clays were kindly supplied without charge by the Baroid Mining Company (montmorillonite) and the Minerals and Chemicals Corporation of America (attapulgite). The polymers likewise were supplied at no cost by the Monsanto Chemical Company (VAMA) and the General Aniline and Film Corporation (the PVM/MA Half Amides).

The numerical value of B_w may be obtained by (a) measuring the inner dimensions of the viscosimeter or (b) solving the equation for B_w after measurement of $d(\log_{10} h)/dt$ for liquids of known viscosity. After many measurements by both methods and the use of water, aqueous glycerol and sucrose solutions in method (b), the second method was accepted as the most reliable and the constant B_w was evaluated, using water at 30 °C. Flow times were measured with a stopwatch having a "split second" following hand. The flow velocity was always held sufficiently low that a kinetic energy correction was unnecessary. A distinct advantage of this viscosimeter is that the

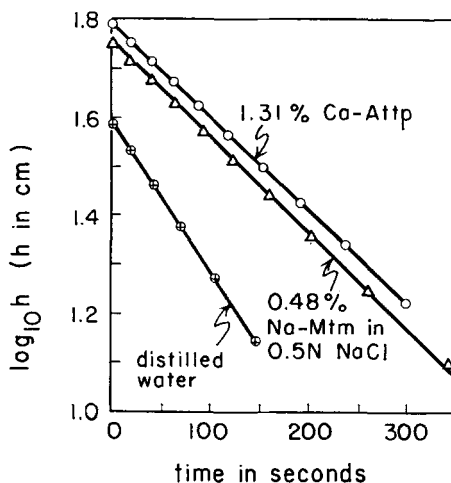


FIGURE 1.—Results obtained with suspensions of homoionic clays and distilled water using the capillary viscosimeter of Maron, Krieger and Sisko (see eq. 3).

density of the liquid or suspension of unknown viscosity is not required in the absolute viscosity calculation and need not be known.

The reliability of the viscosity measurements obtained with the viscosimeter and by means of eq. (3) are illustrated, for distilled water and two different clay suspensions, in Fig. 1. The graph shows $\log h$ in relation to time. A non-Newtonian tendency appears for the 0.48 percent suspension of montmorillonite in 0.5 N NaCl at about $h = 12.5$ cm, or a maximum shearing stress of over 15 dyn/cm² in the capillary.

Preparation of Clay Suspensions

The clays were titrated, first with 0.1 N HCl to pH 3.5 and washed free of chlorides, then with 0.1 N NaOH to pH 7.5 to 8.0 and shaken overnight. More than 95 percent of the $< 2 \mu$ fraction from this Na-saturated material was separated by repeated sedimentation, concentrated by filtration and stored in stoppered Pyrex flasks. This was the stock supply from which samples were taken as needed to produce the desired homoionic forms.

Homoionic substitution was effected (1) by conversion to H-clay by contact with H-ion-saturated Dowex 50 W-X 12, and (2) replacement of H-ion with Na^+ , Ca^{2+} or Al^{3+} , either by carbonate-free titration (to give Na- and Ca-clay) or passage through appropriately saturated Dowex resin (Al-clay).

Preparation and Pre-treatment of Clay-Polymer Complexes

The relative viscosity of solutions of the two polymers, VAMA and PVM/MA-30, was found to decrease with increasing number of measurements made upon them, the decrease being more marked with the former.

Thus, the twenty-second measurement of a 0.04 percent aqueous solution of VAMA gave $\eta_{\text{rel}} = 1.490$, the initial value having been 1.830. The decrease is linear with number of measurement rather than with time. No explanation was obtained. It is unlikely that the repeated shearing stress during flow caused fracture of polymer particles. The same changes were observed with a simple Ostwald viscosimeter thus excluding the possibility of an effect caused by interaction with the driving fluid (mercury) used in the instrument. It is possible that water solutions of pure polymers in these concentrations behave as non-Newtonian liquids. It may be observed that, at 0.1 percent concentration, PVM/MA-30 has a relative viscosity more than five times as great as VAMA solution [$\eta_{\text{rel}}(\text{VAMA}) = 1.062$] of equal concentration.

After several methods of preparing suspensions of the polymer-on-clay complexes for viscosity measurement had been examined, the most satisfactory was found to consist of adding the polymer solution to the clay suspension in the required proportions, shaking the mixture for 1 hr, leaving undisturbed for 24 hr and again shaking for $\frac{1}{2}$ hr prior to the viscosity measurement. The amounts of polymer added per gram of clay and the 24-hr period of contact between clay and polymer allowed for completion of the adsorption process (Mehta, 1956) and also for cessation of increase in viscosity. Such increases were rapid immediately after mixing, with or without shaking, but practically ceased within 24 hr (Fig. 2).

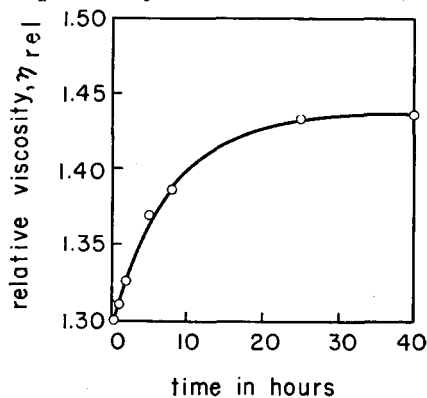


FIGURE 2.—Effect of time of shaking on the relative viscosity of H-Mtm-VAMA.

RESULTS

Viscosity Measurements of H-, Ca-, and Al-Montmorillonite in Relation to Amount of Added VAMA

Curves showing the viscosity number of suspensions of the Al-Mtm-VAMA complexes in relation to specific viscosity are given in Fig. 3. Each curve is labeled with the amount of added VAMA, which ranged from 0 to 2.63 g/100g clay. Note that the concentration of clay in any given suspension may be

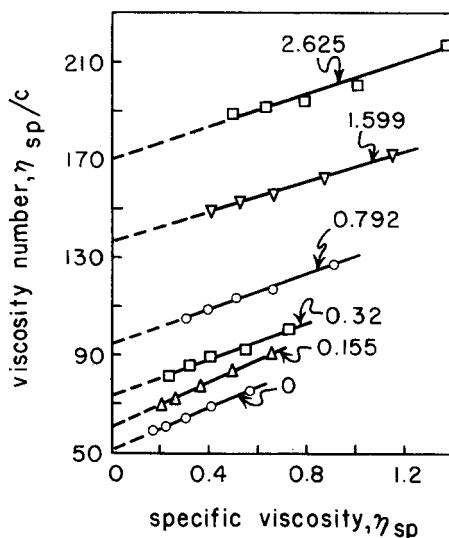


FIGURE 3.—Viscosity number in relation to specific viscosity of suspensions of Al-Mtm-VAMA. Curves are labeled with the amounts of added VAMA, as grams per 100 g of clay.

calculated rapidly by dividing the viscosity number into the specific viscosity.

There is a general similarity between these curves and those for H- and Ca-Mtm, which are not shown, although the amount of adsorbed VAMA was found to have a less pronounced effect on the viscosimetric constants of the calcium montmorillonite than on the other two. The intrinsic viscosity, the interaction index and the specific viscosity, η'_{sp} , at one percent clay concentration ($c = 0.01$) were calculated for all suspensions and the relationships of these constants to the amount of adsorbed VAMA are shown in Figs. 4, 5 and 6. It is evident that the influence of adsorbed VAMA on the constants depends upon the kind of exchangeable cation on the clay and that both $[\eta]$ and k for the H- and Al-Mtm-VAMA suspensions are somewhat similarly affected, although this is a matter of kind rather than degree. The Ca-complexes, however, behave quite differently.

The particular chemical relationships of Al- and H-clays (Low, 1955) suggest that some similarity might be observed in their suspension viscosities, after VAMA adsorption. However, Mehta (1956) concluded that lattice Al and exchangeable Al are equally important in the adsorption of VAMA. If this is so the amount of VAMA adsorbed by Al-clay might be ex-

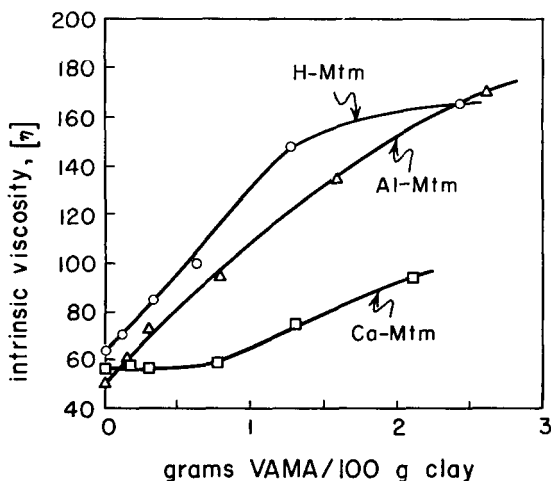


FIGURE 4.—Intrinsic viscosity of suspensions of H-, Ca- and Al-Mtm-VAMA in relation to amount of added polymer.

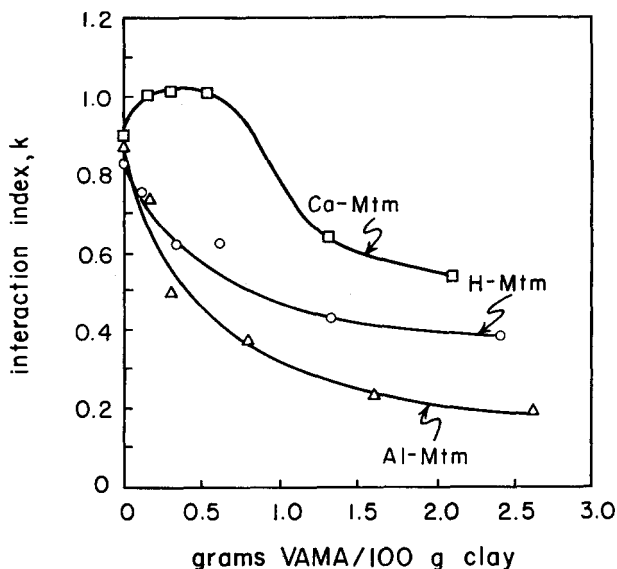


FIGURE 5.—Interaction index of suspensions of H-, Ca-, and Al-Mtm-VAMA in relation to amount of added polymer.

pected greatly to exceed that of H-clay and correspondingly to influence the viscosity constants.

The intrinsic viscosities, interaction indices and specific viscosities at 1 percent clay concentration are consistently higher for the H-Mtm-VAMA than they are for the Al-Mtm-VAMA complexes.

The magnitudes of the viscosimetric constants and the positions of the adsorption sites of the clays may now be used to throw light upon the

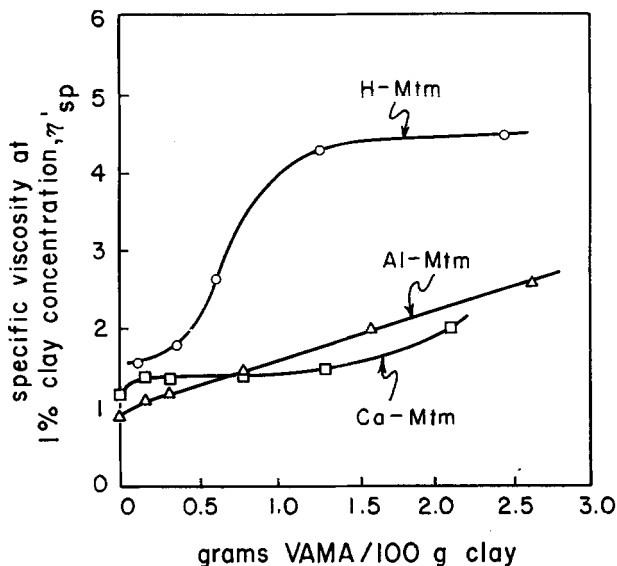


FIGURE 6.—Specific viscosity of one percent suspensions of H-, Ca- and Al-Mtm-VAMA in relation to amount of added polymer.

probable structure of the clay-VAMA complexes. Considering the intrinsic viscosity and interaction, it is observed that:

$[\eta]_{\text{H}} > [\eta]_{\text{Al}}$: a higher dissymmetry of the suspended units of H-Mtm-VAMA is indicated. This corresponds to extension of the length of unit in the direction of either or both of the *a*- and *b*-axes.

$k_{\text{H}} > k_{\text{Al}}$: indicating higher electrical interaction between the units of H-Mtm-VAMA and/or higher hydrodynamic interaction caused by higher dissymmetry.

Since, for both the H- and the Al-complexes, *k* diminishes as polymer adsorption increases (Fig. 5) the increased adsorption of VAMA must be accompanied by decreases in either or both kinds of interaction. Fig. 4 shows, however, that $[\eta]$, and hence the dissymmetry of the units, increases with increased adsorption of VAMA and it must be concluded that the

decrease in k is caused by a decrease in electrical interaction as more of the polymer is adsorbed.

Owing to the great importance (Mehta, 1956) of the Al-bond mechanism, more numerous bonding opportunities exist for the polymer in the presence of Al-Mtm than are offered by the H-Mtm. In the presence of either, bonds may form between VAMA-carboxyls and the lattice Al at the broken edges of the clay platelets. In the presence of Al-Mtm, however, additional opportunities exist at the flat surfaces, so that in this case both exchangeable Al and lattice Al may participate in the formation of Al—OOC bonds. Thus, if Al—OOC bond formation contributes to a decrease in electrical interactions between units, viscosity measurements would be expected to show a greater decrease in k for Al-Mtm-VAMA than for H-Mtm-VAMA. This actually was found to be the case (Fig. 5).

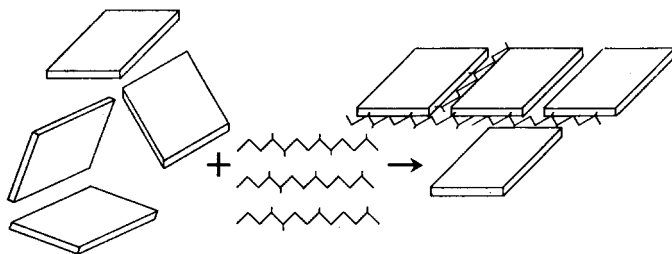


FIGURE 7.—Schematic representation of probable structure of H-Mtm particles linked by VAMA.

It appears that the only way in which H-Mtm particles can be linked together by VAMA during its adsorption so as to give larger units of higher dissymmetry (Fig. 4) is by bond formation on lattice Al at the crystal edges, as represented schematically in Fig. 7. Vertical face-to-face stacking of platelets is not considered to be the mechanism in this case. Nor is it probable that the polymer molecules would be adsorbed at the interplanar spaces of the montmorillonite since this would increase the c -axis spacing. No effect of added VAMA on c -axis spacing could be found by Hagin and Bodman (1954).

Adsorption of VAMA on Al-Mtm may occur at both edges and flat surfaces of particles, where exchangeable Al may also form Al—OOC bonds. An additional bonding mechanism thus exists whereby an exchangeable Al on the flat surface of one platelet is bound to one carboxyl of the polymer and another Al—OOC bond is formed on the surface of a neighboring platelet, involving another exchangeable Al and another carboxyl elsewhere on the same polymer molecule, and so on. Fig. 8 schematically illustrates vertical stacks of clay particles linked in this fashion. By such linkage single, thin platelets combine to form blocky aggregates of reduced dissymmetry.

But it must be concluded that edge-to-edge linkage predominates in the Al-Mtm-VAMA units since the average dissymmetry is increased by the adsorption of greater amounts of VAMA (Fig. 4) although, as pointed out earlier, the intrinsic viscosity of the Al- is less than that of the H-complexes.

As judged by specific viscosity measurements alone (Fig. 6) Ca-Mtm-VAMA appears to be similar to Al-Mtm-VAMA, but consideration of the basic viscosimetric constants indicates that this is not the case. Adsorbed VAMA in amounts less than 0.6 to 0.8 g/100 g Ca-Mtm are almost without effect upon either the $[\eta]$ or k of Ca-Mtm suspension units but $[\eta]$ increases and k decreases when VAMA adsorption exceeds this limit. The early delay in adsorption may be due to the initial high pH (Mehta, 1956). Continued addition of VAMA reduces the pH owing to dissociation of carboxyl groups of the polymer and so promotes adsorption. Here, also, interpretation of

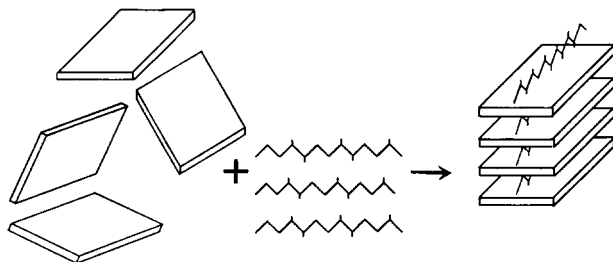


FIGURE 8.—Schematic representation of possible structure of Al-Mtm particles linked by VAMA.

the viscosimetric constants leads to the conclusion that, although edge-to-edge linkage and “stacking” may occur, the former predominates and Ca ions play a minor role in the linkage process. This is in agreement with Mehta’s (1956) hypothesis that divalent linkage is probably not as important as it was once thought to be (Martin *et al.*, 1955) and with Geoghegan’s (1950) observations that alginic acid and pectin had no effect on the aggregation of soils high in Ca- and Na-clays, but a marked effect on soil containing H-clay.

Relation of pH to the Viscosimetric Constants of Montmorillonite-VAMA Complexes

Freshly prepared suspensions of H-Mtm were brought to pH values of from 3 to 10 by addition of 0.1 N NaOH. Equal amounts of 0.1 percent VAMA solution were then added to provide 2 g VAMA/100 g clay and viscosity measurements made as usual. Changes in pH were accompanied by increased adsorption of Na⁺ and it is probable that a pure Na-montmorillonite was formed at pH 10.

There were considerable differences in $[\eta]$, k and η'_{sp} over the whole range in pH. The relation between pH and $[\eta]$ is shown in Fig. 9.

Mehta observed diminishing adsorption of VAMA with increasing pH. Our measurements indicated a high, maximum dissymmetry ($[\eta] = 175$) at pH 6 to 8. According to Mehta's results with montmorillonite VAMA adsorption at pH 6 to 8 was slightly more than 50 percent of the maximum, which he obtained at pH 2.5. Above pH 8 the dissymmetry sharply decreased, perhaps as a result of repulsion between polymer chains and clay particles, both negatively charged, and consequent diminished adsorption.

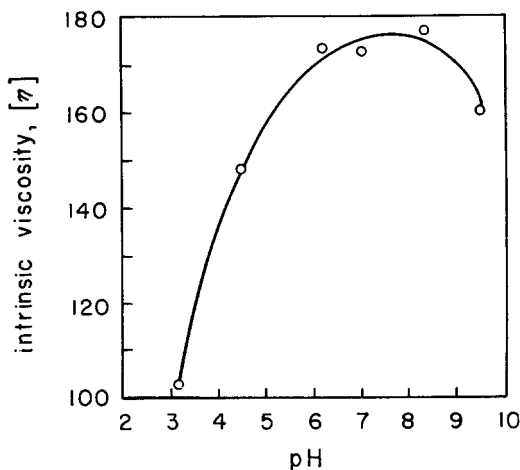


FIGURE 9.—Intrinsic viscosity of montmorillonite-VAMA complex as affected by pH of suspension.

Viscosity of H-Attapulgit in Relation to Amount of Added VAMA

The interaction indices were noticeably high ($1.09 < k < 4.92$) and H-attapulgit flocculated upon the addition of only small amounts of VAMA. Viscosity measurements, therefore, had to be made with suspensions of low concentrations. Owing to the uncertain validity of eq. (3)—for which $c = 0.01$ g/ml—the specific viscosity, η'_{sp} , was calculated from the equation: $\eta'_{sp} = [\eta]/200 - m$. Here $c = 0.005$ g/ml and Newtonian flow is assured. The viscosimetric constants are given in Table 2.

Structure formation can again be deduced from changes in the viscosimetric constants as the ratio VAMA:clay increases. Initially, the constants all increase. This increase points to increased dissymmetry of the units, *i.e.* an end-to-end linkage, by polymer molecules, of the needlelike particles of attapulgit. The intrinsic viscosity, and hence the dissymmetry, diminish upon further addition of polymer and it is concluded that the long units and

individual clay particles now link edge-to-edge. The process is shown schematically in Fig. 10.

The interaction index increases and remains high with increasing quantity of VAMA. This is the result of strong electrical interaction which finally leads to gelation, a point that is confirmed by the unreliability of an extrapolated value of η'_{sp} above the ratio VAMA:clay = 0.034.

TABLE 2.—VISCOSIMETRIC CONSTANTS OF H-ATTAPULGITE-VAMA COMPLEXES

g VAMA/100 g Clay	$[\eta]$	k	η'_{sp}
0	47.0	1.09	0.316
0.27	60.0	1.21	0.472
0.45	64.4	1.11	0.502
1.08	49.5	1.82	0.445
3.41	26.6	4.92	0.384

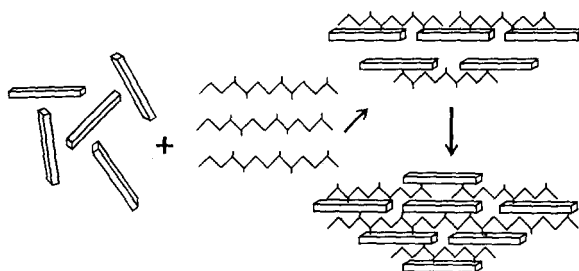


FIGURE 10.—Schematic representation of probable structures of H-Attp particles linked by VAMA.

Viscosity of H-Montmorillonite-PVM/MA Half Amide Complexes

Two copolymers of methyl vinyl ether and maleic anhydride, PVM/MA Half Amide-5 and PVM/MA Half Amide-30, differing in degree of polymerization, were added to H-montmorillonite suspensions in different polymer:clay ratios. Solutions of 0.1 percent PVM/MA-5 and 0.01 percent PVM/MA-30 were prepared and added in the required amounts. It was necessary to use the low concentration of PVM/MA-30 owing to its high degree of polymerization. The viscosimetric constants were obtained in the usual way. Fig. 11 shows the curves relating the viscosity number to the specific viscosity of suspensions of montmorillonite-PVM/MA-30. The viscosimetric constants for these complexes are given in Table 3.

A comparison of the data of Table 3 with the constants obtained for H-Mtm-VAMA (Figs. 4, 5 and 6) indicates that: (a) the intrinsic viscosities of H-Mtm-PVM/MA-30 and -5 extend over a range of values lower than

those of the H-Mtm-VAMA complexes; (b) the specific viscosities of 1 percent suspensions (η'_{sp}) of the H-Mtm-PVM/MA complexes are very much higher, for a given polymer:clay ratio, than are those of the H-Mtm-VAMA complexes. (Note that the validity of η'_{sp} values for Half Amide Type 5 did not

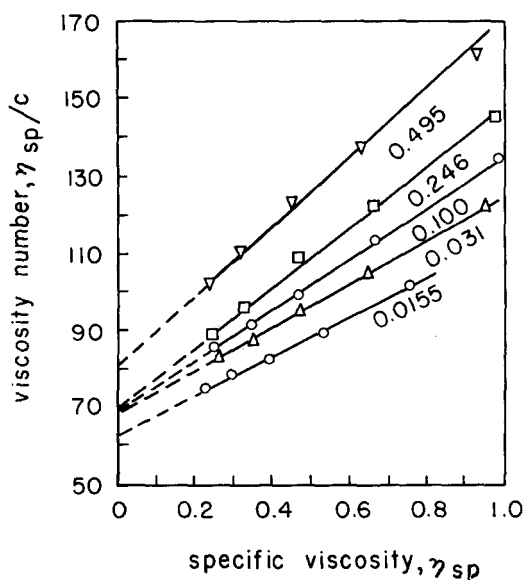


FIGURE 11.—Viscosity number in relation to specific viscosity of suspension of H-Mtm-(PVM/MA Half Amide-30). Curves are labeled with the amounts of added polymer, as grams per hundred grams of clay.

TABLE 3.—VISCOSIMETRIC CONSTANTS OF H-MONTMORILLONITE-PVM/MA-30 AND H-MONTMORILLONITE-PVM/MA-5 COMPLEXES

Complex	g Polymer per 100 g Clay	$[\eta]$	η'_{sp}	η''_{sp}	k
H-montmorillonite--PVM/MA-30	0.0153	63.6	1.257	0.422	0.776
	0.031	68.3	1.542	0.473	0.815
	0.100	68.8	2.036	0.514	0.962
	0.246	70.0	3.335	0.579	1.129
	0.495	80.0	8.89	0.734	1.138
H-montmorillonite--PVM/MA-5	0.214	65.6	2.17	0.504	1.064
	0.558	66.3	2.70	0.532	1.138
	1.113	68.0	8.09	0.628	1.347
	1.835	71.6	—	0.716	1.399
	3.60	83.2	—	0.934	1.327
	5.04	94.0	—	1.040	1.166

extend to a polymer:clay ratio of 1.8 or higher and that the specific viscosity of 0.5 percent suspensions (η_{sp}') accordingly were calculated and are reported in Table 3); (c) the interaction indices accompanying adsorption of both of the half amides on montmorillonite are considerably higher than those caused by adsorption of VAMA; (d) the interaction index increases with increase in adsorption of PVM/MA-30, and over much of the range with PVM/MA-5 but, for the latter, it later declines as the amount of adsorbed VAMA increases.

The lower intrinsic viscosities of the PVM/MA complexes compared with those of the H-montmorillonite-VAMA do not necessarily exclude the possibility of formation of edge-to-edge linked units. The intrinsic viscosities represent an approximation to the average dissymmetry of the suspended units. In the event that particles of both high and low dissymmetry are present in a given suspension an intermediate intrinsic viscosity will be obtained. This was found to be the case with mixtures of suspensions of montmorillonite and kaolinite although their individual intrinsic viscosities are distinctly different.

The important effect of the degree of polymerization of the adsorbed polymer upon particle linking and structure formation becomes clear by comparison of η_{sp}' , η_{sp}'' and $[\eta]$ for the two PVM/MA complexes. For given polymer:clay ratios these parameters are higher for the higher polymer, PVM/MA-30. It is probable that the longer molecules of PVM/MA-30 allow a longer "free chain" for adsorption on additional particles after adsorption has taken place on the first clay particle (Michaels, 1954; Hedrick and Mowry, 1952).

The presence, in the PVM/MA polymer, of two active groups, one carboxyl and one amide group per monomer, introduces some interesting bonding opportunities. The amide groups can form hydrogen bonds with the oxygen ions at the flat surface of the clay platelets (Michaels, 1954) and the carboxyl group can combine with lattice aluminum as before. Several possibilities present themselves, the basic mechanisms being (a) surface-to-surface linkage by hydrogen bonds; (b) surface-to-edge linkage, involving hydrogen bonds of the polymer with oxygens of the flat surface, and carboxyl bonds of the same polymer molecule with the lattice Al of the edge (Al-OOC) of another particle; and (c) edge-to-edge linkage by Al-OOC bonds. These three mechanisms may create units having the structures shown schematically in Fig. 12 (a), (b) and (c). Many complicated structures may develop from these; one possible arrangement which represents a combination of (a) and (c) is given in Fig. 12 (d).

Edge-to-edge linkage will explain the observed increase of $[\eta]$ with increased adsorption of PVM/MA. Also, an explanation for the smaller magnitudes of $[\eta]$ after PVM/MA adsorption, than for $[\eta]$ after VAMA adsorption, is suggested by the probable contemporary formation of other structural

units of lower dissymmetry [*e.g.* types (a) and (b) in Fig. 12] in the case of the PVM/MA. The higher k values, for PVM/MA compared with VAMA, may be caused by heterocoagulation of this kind which is the result, in turn, of the presence of the amide groups in the polymer.

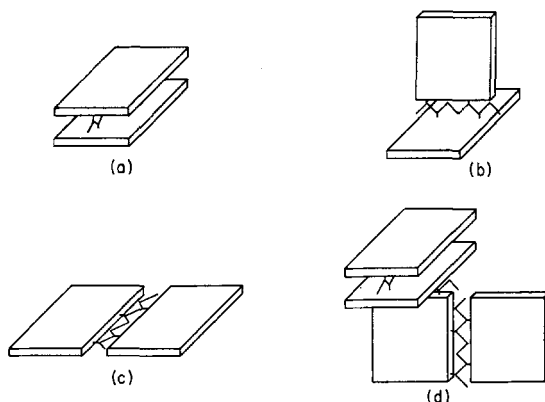


FIGURE 12.—Schematic representation of probable structures of H-Mtm particles linked by PVM/MA Half Amide-30.

The strongly bound, but irregular, structural forms created by heterocoagulation may be expected to occlude water and to resist rupture by shearing forces of the magnitude applied during viscosity measurement. Water occlusion, in effect, would produce a more concentrated suspension than would be apparent from the known mass ratios and contribute to the particularly high η'_{sp} and η''_{sp} values that were observed. These high values strongly support Michaels' earlier findings that the flocculating ability of the polymer is much enhanced by the presence of the two active groups: carboxyl and amide.

CONCLUSIONS

The intrinsic viscosity and interaction factor of dilute aqueous suspensions of montmorillonite and attapulgite, computed from specific viscosity measurements by means of the Schulz-Blaschke equation, are useful indicators of the mechanisms involved in binding organic polymers to clay particles. They provide information on the probable structures created by polymer-on-clay adsorption and the comparative effectiveness of different polymers in causing such changes. The proposed structures agree well with the chemical and mineralogic composition of the clay, and with earlier suggestions concerning linkage mechanisms. Vinyl acetate maleic anhydride (VAMA) and the copolymer methyl vinyl ether and maleic anhydride half amide 30 (PVM/MA-30) are particularly effective binding agents.

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