

Bentonite-Cellulose Systems: Flow Behavior of Mixed Dispersions and Mechanical Properties of Composite Films

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Abstract □ Bentonite and microcrystalline cellulose are used as thickening agents and binders; their interaction was studied in suspension and in the solid state. Mixtures of the two solids covering the whole range of compositions were prepared by blending their aqueous suspensions under high shear. The rheological behavior of the mixed suspensions and the mechanical properties of composite films prepared by drying thin layers of these suspensions were investigated as a function of composition. Based on the volume-percentage of the dry components, bentonite was about five times more effective in increasing the viscosity of aqueous suspensions than cellulose. Cellulose tended to produce yield values. Bentonite formed strong films when its aqueous suspensions were dried; neither pure cellulose nor a mixture containing 88 vol. % cellulose formed coherent films. In the range of 0-77 vol. % cellulose, the in-plane and perpendicular tensile strengths of the composite films decreased only moderately with increasing cellulose content.

Keyphrases □ Bentonite-cellulose systems—flow behavior, mechanical properties □ Cellulose-bentonite systems—flow behavior, mechanical properties □ Films, bentonite-cellulose—relative composition effect □ Rheological behavior, bentonite-cellulose suspensions—relative composition effect

Bentonite and finely dispersed cellulose are used as thickening agents and binders in suspensions, ointments, and tablets (1, 2). The rheology of aqueous bentonite dispersions (3-5) and cellulose suspensions (6, 7), as well as the film-forming ability of sodium bentonite (8), has been reported. The present work deals with the flow behavior of mixed dispersions, containing varying proportions of cellulose and clay, and with the mechanical properties of films prepared therefrom. The purpose was to determine whether there is any synergism in thickening and binding; for instance, whether partial replacement of bentonite by cellulose boosts the viscosity of bentonite suspensions, or whether the presence of cellulose increases the strength of solid bentonite. The interaction between clays and cellulose is described in previous work (9, 10).

EXPERIMENTAL

Materials—Microcrystalline cellulose¹ is manufactured by acid hydrolysis of wood pulp with a high α -cellulose content to the "level-off degree of polymerization," followed by mechanical disintegration (11, 12). Suspensions were made by dispersing the powder in water with a Waring blender. They were permitted to hydrate 24 hr. before admixing clay dispersions.

Sodium bentonite² was slurried in a Waring blender with water for 10 min. at top speed and was decanted from settled out grit and heavy particles. This reduced the clay concentration from 28 to 21 g./l. The supernatant dispersion was passed through a column of a commercial cation-exchange resin³ in the sodium form. The pH of a dispersion containing 21 g./l. was 9.8. Since the micro-

crystalline cellulose is partly soluble in alkaline media, the pH of the clay dispersion was adjusted to 5-7 as follows: a small amount of the sodium bentonite dispersion was passed through a column of the cation-exchange resin in the hydrogen form, which reduced its pH to 2.2. It was then mixed immediately with enough of the sodium form to obtain the desired pH.

The water was twice distilled. Neither bentonite nor cellulose contained water-soluble impurities. Mixed suspensions were prepared by combining the required amounts of clay dispersions and cellulose suspensions of known concentrations and stirring together in a Waring blender, followed by two passes through a hand homogenizer. Lower viscosities and yield values were found if homogenization was omitted. The total solids content of dispersions was sometimes determined by drying at 125° to ensure against concentration changes due to evaporation of water. The nominal and actual compositions always agreed within $\pm 0.01\%$, expressed as solids content.

After viscosity measurements, the suspensions were concentrated, spread into thin layers on metal or glass trays, and dried in a forced-circulation oven. As a routine precaution, the composition of a few films was determined from the ash content at 600°. The difference between nominal and actual composition was always below 0.1% in terms of percentage composition values. This shows that preferential settling out of bentonite or of cellulose from the suspensions during handling did not occur.

Methods—Viscosity measurements were made with a rotational Synchro-Lectric viscometer,⁴ using chiefly the No. 1 and occasionally the No. 2 spindle. The instrument was used at 2, 4, 10, and 20 r.p.m. with the guard in place. The 650-ml. samples were measured in 800-ml. beakers. All measurements were made at 22-23.5°.

Because the viscosity of suspensions containing cellulose rose very rapidly even after short rest periods, the flow measurements had to be restricted to those observable after elimination of thixotropic thickening. Reproducible results were obtained when the suspensions were stirred for 10 min. with a magnetic stirrer at top speed immediately before measuring viscosities. Sometimes, thixotropic increases in viscosity occurred even during viscosity measurements. In those cases, the suspensions were stirred between readings as often as was necessary to obtain reproducible values.

Flow curves were drawn as revolutions per minute (rate of shear) versus scale divisions of torque (shear stress); the full scale was 500 divisions. Yield values, Y , are reported as scale divisions for No. 1 spindle at the point where the extrapolated flow curve intersected the shear stress axis. They are only approximate values, particularly for those systems where rapid thixotropic buildup of viscosity introduced some uncertainty in the readings at 2 r.p.m.

There are two convenient and representative ways of defining the viscosity of shear-thinning liquids, some of which have yield values. The first, "differential viscosity," is defined here as the reciprocal slope of the secant to the flow curve at the points for 10 and 20 r.p.m. Since the instrument had only four speeds, this was more reproducible than drawing the tangent to the flow curve at a given r.p.m. and using its reciprocal slope (13, 14). The differential viscosities, η_{diff}^* , in centipoises (cps.), were calculated as

$$\eta_{diff}^* = K(\Delta \text{ div.}/\Delta \text{ r.p.m.}) \quad (\text{Eq. 1})$$

which became

$$\eta_{diff}^* = 1.96 \left[\frac{\text{div.} (20 \text{ r.p.m.})}{1.06} - \text{div.} (10 \text{ r.p.m.}) \right] \quad (\text{Eq. 2})$$

¹ Avicel-PH, FMC Corp., Marcus Hook, Pa.

² Volclay bentonite, 325 mesh, American Colloid Co., Skokie, Ill.

³ Amberlite IR-120, Rohm & Haas Co., Philadelphia, Pa.

⁴ Model RVF, Brookfield Engineering Laboratories, Inc., Stoughton, Mass.

for the No. 1 spindle, and

$$\eta_{dic}^* = 8.2 \left[\frac{\text{div. (20 r.p.m.)}}{1.17} - \text{div. (10 r.p.m.)} \right] \quad (\text{Eq. 3})$$

for the No. 2 spindle; div. (20 r.p.m.) is the number of scale divisions on the torque scale ranging from 0–500 at the speed of 20 r.p.m. The numerical constants were determined by calibrating the instrument with a 60% sucrose solution (48 cps. at 23.2°).

A second way of describing the flow behavior is as “apparent plastic viscosity” (15), by analogy to plastic and pseudoplastic liquids (16). Apparent plastic viscosities, η_{pl}^* , in cps., for the No. 1 spindle were calculated as

$$\eta_{pl}^* = \frac{\text{div. (20 r.p.m.)} - Y}{1.06} \quad (\text{Eq. 4})$$

This is the reciprocal slope of the secant to the flow curve at the point of 20 r.p.m. and the yield value or, if $Y = 0$, at the origin. Such computations are necessary because, while the suspensions containing only cellulose gave nearly linear flow curves above the yield value between 4 and 20 r.p.m., many of the suspensions containing clay gave flow curves that were convex toward the shear stress axis, and the two kinds of curves must be compared. For Newtonian liquids, differential viscosity and apparent plastic viscosity are identical with the Newtonian viscosity.

The mechanical properties of the films were measured after conditioning at 23° and 50% relative humidity, using a recording stress-strain tester equipped with strain gauges.⁵ Tensile strength in the plane of the film (x - y direction) was determined on strips 1.27 cm. (0.5 in.) wide and with a 2.54-cm. (1.0-in.) distance between the clamps, which were elongated at the rate of 2%/min. To compensate for differences in density, the tensile strength is expressed as breaking length, *i.e.*, the smallest length of film sufficient to cause it to break under the load of its own weight. The tensile strength perpendicular to the plane of the film (z -direction) was determined by gluing a 2.54 × 2.54-cm. (1 × 1-in.) film specimen with epoxy cement between two cubic aluminum blocks of 2.54-cm. (1-in.) side length, attaching one to the upper jaw of the tensile testing machine and the other to the crosshead, and lowering the latter at the rate of 0.025 cm./min. (0.01 in./min.). The z -direction tensile strength represents resistance to delamination. The epoxy cement did not appreciably penetrate the clay film because, except for the layer immediately adjoining the aluminum surface, the ruptured films swelled and dispersed freely in water.

RESULTS

Flow Properties—Typical flow curves are shown in Fig. 1. Differential and apparent plastic viscosities and approximate yield values are listed in Table I. Compositions are expressed as volume percent of dry material, with a density of 1.5 g./cm.³ for cellulose, 2.8 g./cm.³ for clay, and 1.0 g./cm.³ for water. Yield values are expressed as scale divisions for the No. 1 spindle, full scale being 500 divisions. As indicated by Table I, clay tends to build up viscosity faster than cellulose, and cellulose tends to produce yield values faster than clay with increasing concentration.

The effect on the differential viscosity of gradually replacing clay with microcrystalline cellulose while maintaining the total concentration of suspended solids constant at 1.64 vol. % of dry material is shown in Fig. 2. Also shown is the effect of concentration on the differential viscosity of dispersions of pure clay. The abscissa scale representing clay concentration is the same for both curves. Therefore, the upper, broken curve refers to compositions containing a concentration of cellulose equal to 1.64 vol. % minus the indicated clay concentration.

If the two curves coincided, microcrystalline cellulose would have the same thickening effect on clay dispersions as water, *i.e.*, none. If the broken curve representing the viscosity of mixed suspensions at constant total concentration was a straight horizontal line located at the differential viscosity of a pure clay dispersion containing 1.64 vol. %, namely 135 cps., cellulose would have the same thickening effect on clay dispersions as an equal volume of additional clay. The broken curve was only slightly above the solid

Table I—Differential Viscosities, Apparent Plastic Viscosities, and Yield Values for Suspensions Containing Na⁺/H⁺ Bentonite and/or Microcrystalline Cellulose

Clay, vol. %	Cellulose, vol. %	Differential Viscosity, cps.	Apparent Plastic Viscosity, cps.	Yield Value, Five-Hundredths of Full Scale
0.730	0	13	11.5	0
0.864	0	16	15	0
1.024	0	19	18.5	0
1.118	0	22	23	0
1.199	0	26	30	0
1.213	0	28	32	0
1.317	0	33	41.5	1
1.430	0	47	64	2
1.552	0	78	108	9
1.650	0	135	194	22
0	1.616	7	7	0
0	3.149	9	11	9
0	3.252	10	13	7
0	3.355	11	12	8
0	3.430	10	11	9
0	3.459	9	12	10
0	3.562	13	14.5	9
0	3.666	12	18	16
0	3.770	11	19	17
0	3.874	12	21	20
0	3.947	14	18	25
0	3.978	18	28	26
0	4.082	18	23	27
0	4.186	16	25	32
0.182	1.441	11	8.5	0
0.365	1.265	12	10.5	0
0.552	1.087	15	12.5	0
0.736	0.907	18	14	1
0.921	0.727	19	21	1
1.108	0.547	24	28	2
1.299	0.360	41	49	3
1.486	0.183	72	97	9
0.344	3.085	71	—	—
0.257	3.172	44	—	—
0.129	3.294	29	20	56
0.150	3.840	39	40	152
0.300	3.700	107	120 ^a	610 ^a
0.514	2.915	123	140 ^a	550 ^a

^a Divisions measured with No. 2 spindle × 4.

curve, indicating that microcrystalline cellulose exerts only a modest thickening effect on clay dispersions.

The reverse situation is shown in Fig. 3. Starting with a cellulose suspension of 3.430 vol. % and replacing small but increasing amounts with clay at a constant volume fraction of dry solids caused

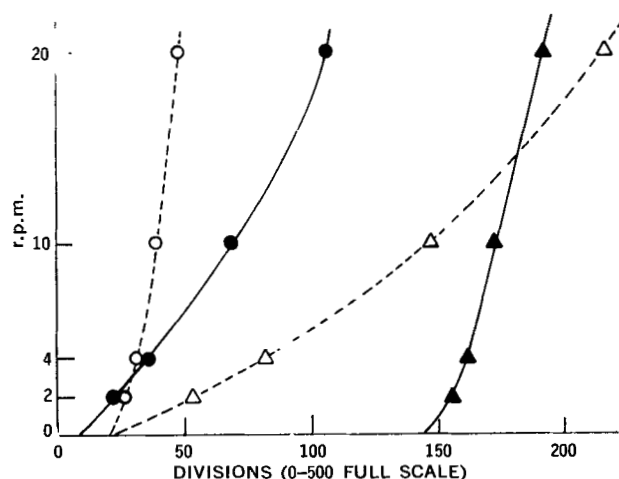


Figure 1—Typical flow curves for suspensions of bentonite, microcrystalline cellulose, and their mixtures. Key: O, 3.874 vol. % cellulose; ●, 1.486 vol. % clay + 0.183 vol. % cellulose; ▲, 3.840 vol. % cellulose + 0.150 vol. % clay.

⁵ Instron Corp., Canton, Mass.

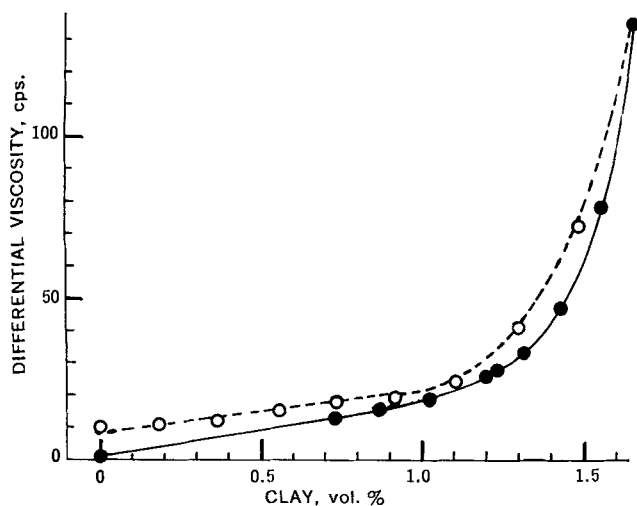


Figure 2—Differential viscosity of clay dispersions as a function of clay content, and the effect of replacing clay with cellulose. Key: ●—●, clay only; and ○—○, gradual replacement of clay with cellulose at a constant solids content of 1.64 ± 0.02 vol. %.

a rapid increase in differential viscosity. In the range of compositions studied, this increase amounted to about 170 cps./vol. % replaced. If the increase in viscosity per volume percent was the same for cellulose as for clay, the broken curve would be a straight horizontal line located at the differential viscosity of the 3.430 vol. % cellulose suspension, namely 10 cps. The rapid divergence of the two curves shows that for suspensions of microcrystalline cellulose, bentonite is a far more effective thickening agent than are additional amounts of cellulose. Similar plots and the same conclusions can be obtained with apparent plastic viscosities.

The following numerical examples show how the relative thickening efficiency of clay and that of cellulose were compared. From Fig. 2, it is seen that a suspension containing 0.47 vol. % clay and $1.64 - 0.47 = 1.17$ vol. % cellulose has the same differential viscosity as a 0.80 vol. % clay dispersion. Therefore, $0.80 - 0.47 = 0.33$ vol. % clay is approximately equivalent in thickening power to 1.17 vol. % cellulose, or 1 vol. % clay is equivalent to 3.55 vol. % cellulose. From Table I, a 4.0-vol. % cellulose suspension is seen to have the same differential viscosity as the interpolated value for a 0.98-vol. % clay dispersion, and a 3.8-vol. % cellulose suspension the same as a dispersion containing 0.73 vol. % clay. The equivalent

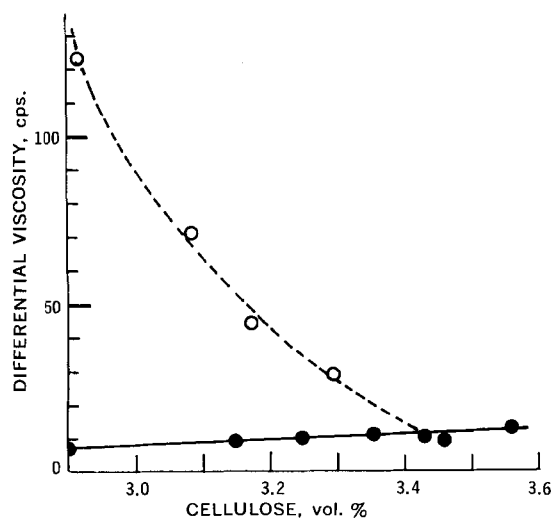


Figure 3—Differential viscosity of cellulose suspensions as a function of cellulose content, and the effect of replacing cellulose with clay. Key: ●—●, cellulose only; and ○—○, gradual replacement of cellulose by clay at a constant solids content of 3.430 ± 0.004 vol. %.

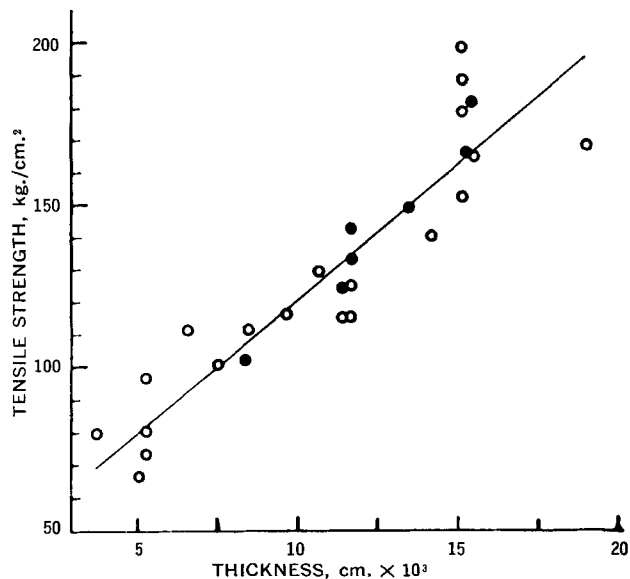


Figure 4—Effect of thickness on the tensile strength of Na^+ bentonite films. Rate of elongation: ○, 2%/min.; and ●, 10%/min.

of 1 vol. % clay is, therefore, 4.08 and 5.20 vol. % cellulose, respectively. The values obtained by this kind of calculation, based on differential viscosities, ranged from 1:3.0 to 1:9.0, with a mean equivalent thickening ratio of 1:4.5 vol. % dry clay–vol. % dry cellulose. Similar calculations for apparent plastic viscosities gave a range of 1:3.2–1:10.8 for equivalent thickening ratios of clay–cellulose and a mean of 1:4.9. The large spread in the values may be due to the fact that the structural mechanism by which bentonite thickens a cellulose suspension is different from the one operative in a dispersion of pure bentonite. The 4.5 and 4.9 ratios are only meaningful as an order of magnitude.

According to Einstein's law, the viscosity of dispersions is determined only by the total volume fraction of the dispersed phase and not by its particle size. The present systems are strongly non-Newtonian; even the viscosity of very dilute bentonite dispersions was found to be 70 times larger than that predicted by Einstein's law, owing to the interaction between particles (5). This interaction is responsible for the pronounced thickening observed. Thickening, *i.e.*, high viscosities and yield values, results from three-dimensional networks formed by particle–particle association. Small particle sizes, as shown by high specific surface areas, and highly asymmetric particle shapes are conducive to thickening (Reference 13, p. 338; Reference 14, p. 180). The increase in viscosity with de-

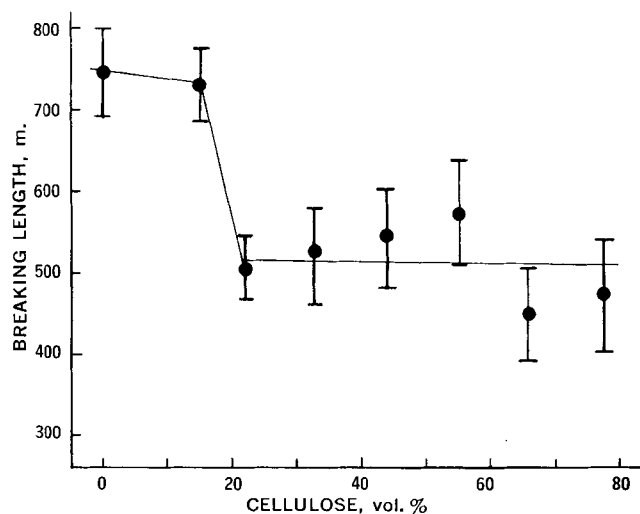


Figure 5—Effect of microcrystalline cellulose on the breaking length of $\text{Na}^+|\text{H}^+$ bentonite films.

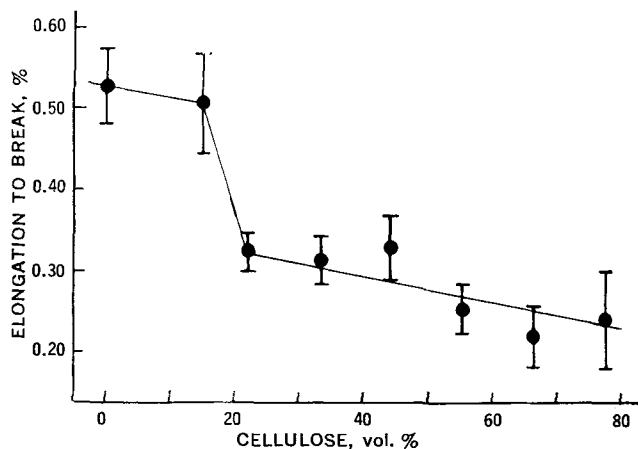


Figure 6—Effect of microcrystalline cellulose on the elongation to break of Na^+/H^+ bentonite films.

creasing particle size has also been attributed to a solvation shell surrounding the particles, which increases their effective volume (17).

The kind of bentonite used here has stacks of 3–4-lattice layers as primary particles. These swell in water by inserting three layers of water, each 3 Å thick, between adjacent clay layers (5, 18). Neglecting the lateral area, the specific surface area corresponding to the basal planes is 240 m^2/g . The primary particles in microcrystalline cellulose, which had been stirred for 10 min. at top speed in a Waring blender and given two passes through a hand homogenizer, were rods or laths with a median length between 4.5 and 6.5 μ and a median diameter or width between 1.0 and 1.6 μ when wet. According to these microscopic measurements, the specific surface area of the water-swollen particles was about 3 m^2/g .

The bentonite lamellas are far more asymmetrical than the rods of microcrystalline cellulose. The higher specific surface area of the clay particles compared to the cellulose particles, and their greater asymmetry, should produce an equivalent thickening ratio far greater than 1:4.5 or 1:4.9. This may indicate the existence of some specific effects which enhance the thickening power of the microcrystalline cellulose or reduce that of bentonite. Hydrogen-bond formation resulting in more and stronger particle-to-particle attachments for cellulose is unlikely to be responsible for the smaller than expected difference in thickening, because bentonite particles can adhere to cellulose surfaces by hydrogen bonds (as proton acceptors) as readily as two cellulose surfaces adhere to each other (9). There seems to be no reason why the hydration shell surrounding a cellulose particle should be substantially deeper than that around a clay particle of the same size. Perhaps electrostatic effects, specifically the repulsive component of the interaction between the more highly charged clay particles, are involved. Another possible explanation is that the mechanical shearing to which the microcrystalline cellulose was subjected, like the beating of paper-making pulp, frazzled the rods, rendering their surface fuzzy. Microfibrils emanating from the rods need not be visible at the magnification of 500 \times used in these microscopic observations, yet they could increase the surface area of these rods and considerably enhance their ability to form three-dimensional networks in suspension. This would also explain why the rods seemed to occur in clumps.

Film Properties—Neither pure microcrystalline cellulose nor a mixture containing 88 vol. % cellulose formed coherent films when their aqueous suspensions were dried without external pressure. For the remaining range of compositions, the apparent densities of the conditioned films, *d*, i.e., the weight divided by length \times width \times thickness, increased with increasing weight % clay (% CL) according to the equation

$$d = 0.544 + 0.0134\% \text{ CL} \quad (\text{Eq. 5})$$

Using 1.5 and 2.8 g/cm^3 as bulk densities of cellulose and clay, the equation indicates that the void volume of the films increased with increasing cellulose content, from 30% for pure clay films to 44% for films containing 77.6 vol. % cellulose. The high void volume associated with microcrystalline cellulose is useful for the

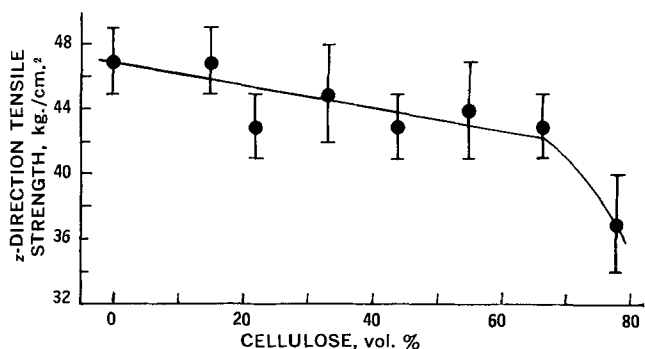


Figure 7—Effect of microcrystalline cellulose on the z-direction tensile strength of Na^+/H^+ bentonite films.

absorption of oils and pharmaceuticals in tablets or gels (2).

The mechanical properties of films of pure clay were found to improve with increasing thickness (Fig. 4). This runs counter to the usual observation of increasing strength of films and fibers with decreasing cross-sectional area owing to the reduced probability of finding flaws. For this reason, only films of thickness between 0.010 and 0.015 cm. were tested in later work. As can be seen from Fig. 4, the proportionality between tensile strength and thickness cannot extend to films much thinner than those studied in the present work. Otherwise, extrapolation of the least-squares line based on films in the thickness range of 50–150 μ would result in a tensile strength of nearly 30 kg/cm^2 for a film of zero thickness. The correlation coefficient between tensile strength (dependent variable) and film thickness for the data of Fig. 4 is 0.909. At 26 degrees of freedom, this corresponds to a level of significance better than 0.1%.

In Figs. 5–7, each point is the average of at least eight measurements, and the bars represent \pm the standard deviation of the averages. The initial 15 vol. % cellulose had no noticeable effects on breaking length and elongation. Higher loadings of cellulose reduced the former by approximately 30% to a nearly constant level independent of cellulose loading. Except for the film containing 77.6 vol. % cellulose, the z-direction tensile strength decreased only very slightly with increasing cellulose content (note the expanded ordinate scale of Fig. 7).

The fact that finely dispersed cellulose lowered the strength of sodium bentonite or hydrogen bentonite films only moderately indicates that the adhesion of cellulose to clay is of the same order of magnitude as the adhesion of clay to itself. The strength of the pure bentonite films indicates that the latter is considerable. Mixed cellulose–bentonite films swelled freely and disintegrated readily in water over the entire range of compositions.

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NOTES

Cautions Regarding the Physical Interpretation of Statistically Based Structure-Activity Relationships

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Abstract □ The distinction between the use of multiple regression analysis as a predictive tool and as a means of investigating controlling physical characteristics in structure-activity studies often is unrecognized. Three examples of complications that can arise with either of these goals in mind are discussed. The first is an illustration of a "false" parabolic dependence of activity on lipophilicity; the second deals with unrecognized interrelationships between certain physical parameters; and the third is a situation where a number of statistically significant correlations can be presented, each of which may be given a differing physical interpretation.

Keyphrases □ Structure-activity relationships—precautions concerning interpretation □ Multiple regression analysis—use, misuse

Within the past few years, multiple regression analysis has been exploited as a statistical tool for the evaluation of structure-activity data. One goal of these analyses is the derivation of a regression equation which will provide estimates of the biological potencies for additional structural entities within a series. A second goal is the determination of the physical and chemical properties of a given series of compounds which are most influential in affecting the observed biological potencies. It is often not recognized that each of these goals represents a separate problem, because the multiple regression approach usually makes use of physically meaningful parameters. As a consequence, any regression equation that correlates structure-activity data can be given a physical interpretation. At times, however, a quirk within a set of structure-activity data can lead to a statistically significant regression equation which provides a poor, if not erroneous, reflection of the physical factors affecting biological potency. At other times, a physical interpretation becomes difficult because a number of correlations can be presented for the same data, each of which involves one or more parameters that could be given a differing physical interpretation. Three examples to illustrate these complications are discussed in this report.

EXAMPLE 1

The minimum inhibitory concentrations against *Escherichia coli* for a variety of congeneric sulfanilamides have been correlated linearly with the Hammett σ -value or with the pKa for the compounds (1, 2). Other congeneric sulfanilamide series have been found (3) which require the addition of π or of π and π^2 terms in a multiple regression model in order to gain a correlation with their bacteriostatic activities. A π term in combination with σ or pKa in a regression equation indicates that lipophilic and electronic factors, respectively, are controlling biological potency. When both π and π^2 appear in a regression equation, the biological activities are parabolically related to the lipophilicities of the compounds; *i.e.*, there is an optimal lipophilicity to observe a maximum biological response within the series.

A reasonable approach to follow if regression equations are to be used as a guide to further syntheses is first to synthesize and test a relatively few compounds which vary over a wide range with respect to their expected electronic (σ) or lipophilic (π) characteristics. If the subsequent regression analysis requires the addition of a physical parameter other than that chosen as an initial criterion to correlate the activity data, it could be said that the additional parameter (or parameters) reflects a real physical requirement for the system under study. Following this approach, *N*¹-benzoysulfanilamides having substituents covering extremes in Hammett σ -values (Compounds 1-7; Table I) are found to have their bacteriostatic potencies correlated by the equation

$$\log(1/C) = -0.81 (\pm 0.16)\sigma + 1.18 (\pm 0.31)\pi \quad (\text{Eq. 1})$$

	(-4.99)	(3.74)	
	-1.19 (± 0.35) π^2 + 5.10		
	(-3.38)		
<i>N</i>	<i>s</i>	<i>R</i>	<i>F</i> (3,3)
7	0.12	0.98	34.67

In Eq. 1, the standard error for the estimate of a coefficient appears in parentheses after the coefficient; in parentheses below the coefficient is the *t* test. The statistics for the equation are the standard error of the estimate *s*, the multiple correlation coefficient *R*, and the *F*-ratio.

Based on Eq. 1, it may be concluded that electronic and lipophilic factors control the bacteriostatic activities for this series of sulfanilamides and that there is an optimum lipophilicity for the series. If the latter conclusion is true, a regression equation based on the activities for a larger number of *N*¹-benzoysulfanilamides should retain the π and π^2 terms as found in Eq. 1, since the lipophilicities for the additional compounds should lie on the same parabola as is found for the smaller series. In this particular instance, an extension