New Instrument for Measuring Structure in Fluids

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A new instrument was developed to study the structural properties of fluids. The instrument consists of a steel sphere suspended from a strain gauge in a fluid sample contained in the core of an electromagnet. Static yield values can be obtained by variation of the electromagnetic field. The behavior of structural fluids in this instrument appears to be in agreement with Bingham's theory on fluid structure.

PREVIOUS EXPERIMENTAL methods designed to evaluate the yield values of suspending agents have involved flow of the sample. Once a flow curve of the sample was obtained, the linear portion of the curve was extrapolated to the stress axis and this intercept taken as the classical the Bingham yield value (1). Figure 1 presents an actual rate of shear *versus* stress curve obtained from the M-2 viscometer (2) for a 0.30% Carbopol-934 mucilage which illustrates the three yield values described by Fischer (3). They are the Bingham yield value, f_B, the value most commonly used in pharmacy; f_L, a lower value which is fixed at the beginning of shear (this is not necessarily laminar flow); and f_m, the maximum yield value which is established presumably by the beginning of laminar flow.

Bingham (4) postulated that a certain portion of the shearing stress was used in overcoming the "internal friction" of the material. He stated that if the material were perfectly elastic, it would undergo elastic deformation at stresses below the yield value. The initial restoring force is zero before stress is applied, then gradually increases to a maximum as the shear force is increased. If the applied force increases beyond the maximum value of the restoring force, flow begins.

In a static system forces must still be acting on the suspended particle even though no flow is occurring. If the forces on the particle can be controlled, then the particle itself can be used to study the physical properties of the suspending agent. One method of controlling forces acting on a particle is through the use of a magnetically susceptible particle. If such a particle is placed in a magnetic field, the downward force exerted by the particle can be controlled by varying the intensity of the field.

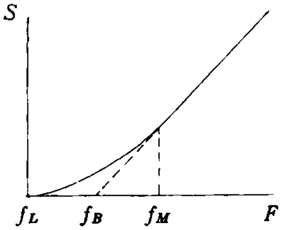

Fig. 1.—Flow curve for a 0.30% Carbopol-934 mucilage illustrates the three classical yield values.

ELECTROMAGNETOYIELDOMETER (EMY)

Figure 2 presents a schematic diagram of the instrument. It consists essentially of a steel sphere attached through a spring to a strain gauge. The sphere is placed in the sample which is contained in the core of an electromagnet. The position of the sphere within the sample can be controlled by adjusting the support of the strain gauge and/or the support of the electromagnet. As voltage is applied to the electromagnet, the sphere is pulled through the sample. The force on the sphere is detected by the strain gauge.

The sphere will descend a lesser distance in a sample of a structural fluid than in a sample of a nonstructural fluid for the same applied voltage, since the structural fluid exerts an additional upward force on the sphere. In a nonstructural fluid there is no additional upward force, and the sphere descends to the point where it is in equilibrium with the upward force of the strain gauge. Thus, the difference between the equilibrium force for a nonstructural fluid and that for a structural fluid is related to the yield value of the structural fluid. This can best be seen by analyzing the forces acting on the sphere.

The force acting downward, $f\downarrow$, is

$$f\downarrow \; = V(\rho_2)\,g + M \qquad \text{(Eq. 1)}$$

where V is the volume and ρ_2 the density of the sphere, g is the gravitational acceleration, and M is the force due to the magnetic field. For a nonstructural fluid the force acting upward, $f\uparrow$, is

$$f\uparrow \; = V(\rho_1)g + F_S \qquad \text{(Eq. 2)}$$

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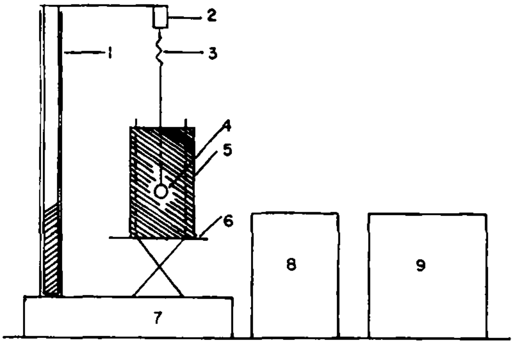

Fig. 2.—The electromagnetoyieldometer. 1, Strain gauge support; 2, Statham transducer, GL-1.5-350, Statham Instruments, Hato Rey, Puerto Rico; 3, spring; 4, steel sphere, diameters 0.635, 0.794, and 1.111 cm.; 5, magnetic wire wound on hollow glass cylinder; 6, laboratory jack; 7, vibradamp, Fischer Scientific Co.; 8, powerstats, type 116, The Superior Electric Co., Bristol, Conn.; 9, Varian recorder, G-10, Varian Associates, Instrument Division, Palo Alto, Calif.

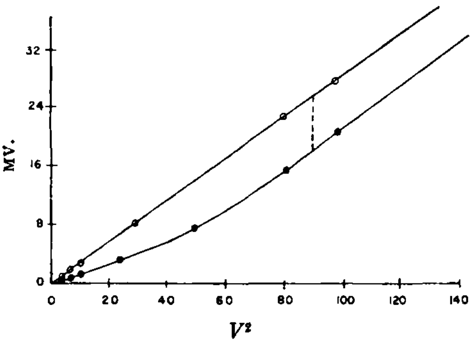

Fig. 3.—A nonstructural fluid, water, (O) compared with a structural fluid, (●) tragacanth supreme mucilage, from data obtained from the electromagnetoyieldometer at high voltages.

where ρ_1 is the density of the sample, and F_S is the upward force of the spring. At equilibrium these forces are equal and

$$F_S = V(\rho_2 - \rho_1)g + M \qquad \text{(Eq. 3)}$$

In the case of a structural fluid the force acting downward is the same as Eq. 1, but the upward force becomes

$$f\uparrow = V(\rho_1)g + F_S + Y \qquad \text{(Eq. 4)}$$

where Y is the resisting elastic force of the fluid. Note that Y will depend on the distance the sphere has moved reaching a maximum just before flow begins. Again, at equilibrium these two forces are equal and

$$F_S = V(\rho_2 - \rho_1)g + M - Y \qquad \text{(Eq. 5)}$$

Therefore, the value for F_S in Eq. 3 is less than the value for F_S in Eq. 5 by the value of Y.

RESULTS OBTAINED WITH THE EMY

The magnetic field intensity is proportional to the square of the applied voltage (5). Therefore, a plot of the force on the sphere (recorded as millivolts) *versus* the square of the applied voltage is linear. Such a plot was designated an EMY curve.

Experiments showed that the sphere could be varied +1 mm. in position with no measurable change in magnetic force. The sphere was allowed to descend no further than 100 μ.

Experimentation was carried out to show that the decrease in force on the sphere in structural liquids was actually due to a structural resistance and not due to a difference in magnetic susceptibility of the liquid or to viscosity. A 0.31% aqueous solution of sodium nitrate, possessing the same viscosity as water but higher ionic strength than the Carbopol-934 solutions, was tested. The EMY curve for this experiment coincided with the EMY curve for water, showing that neither ionic interference or magnetic susceptibility were factors. A sample of 97% glycerin in water whose viscosity was 100 times greater than that of water was studied under the same conditions. The data again showed no difference in the EMY curves.

Experiments did show that the results were very sensitive to temperature changes. As the applied voltage was increased, heating and expansion of the sample occurred. The sample expanded upwards, carrying the sphere with it in the case of structural liquids. This upward movement was detected as a decrease in the strength of the signal from the strain gauge. This heating effect caused resulting EMY curves to bend toward the force axis.

The coefficient of thermal expansion for water at 25° is 64×10^{-6} (degrees^{-1}). Assuming that the temperature is uniform across the core of the electromagnet, a 0.2° temperature change corresponds to a volume change of 1.52×10^{-3} cm.^{3} This would be equivalent to a change in height of the sample in the electromagnet of 15.8 μ. At 3 v. applied potential the sphere moved 50 μ, the error introduced by such a change in height would be approximately 32%. The heating effect was circumvented by applying potentials to the electromagnet rapidly in increments of 2 v. Experimentation ceased when 0.01° change in temperature was noted in a thermistor bridge monitor.

Water was used as the standard nonstructural liquid. Once the linear EMY curve was obtained for water, a structural fluid such as 0.15% Carbopol-934 mucilage was tested under the same conditions. The resulting EMY curve was at first linear with a slope much less than the slope of the curve for water; then it curved upward until it appeared to be parallel to the curve for water. The point where curvature begins can be defined as the elastic limit of the material in analogy to the stress-strain curve of metals. Figure 3 is representative of the EMY curves obtained with structural and nonstructural fluids. The fluids studied were the tragacanth super initial and supreme mucilages and the muci-

Table I.—Yield Values of Selected Mucilages Expressed in Dynes/cm.^{2}

Mucilage	1.111 cm. Diam. Sphere	0.794 cm. Diam. Sphere
Carbopol-934		
0.23%	175.6	161.2
0.15%	34.5	...
Tragacanth		
Supreme	113.0	...
Super initial	124.8	...

TABLE II.—COMPARISON OF YIELD VALUES OBTAINED FROM THE EMY WITH THOSE OBTAINED FROM THE RISING CYLINDER RHEOMETER[a]

	Yield Value			
	Carbopol-934		Tragacanth	
Method	0.15%	0.23%	Supreme	Super Initial
EMY at 25° C.	34.5	175.6	113.0	124.8
Rising cylinder at 30° C.	16.8	131.7	123.4	156.4

[a] Values are expressed in dynes/cm.^{2}

TABLE III.—EFFECT OF TEMPERATURE ON YIELD VALUE[a]

	Temp., ° C.	
Mucilage	30°	26°
Carbopol-934 0.23%	134.5	175.6
Tragacanth super initial	56.5	78.3

[a] The 1.111-cm. diam. sphere was used in the EMY. Values are expressed in dynes/cm.^{2}

lages of Carbopol-934 prepared in the manner previously described (6).

The values of the forces acting on the different sized spheres in the same sample appeared to be approximately in the ratio of the squares of the diameters of the spheres. Because a suspended particle is being acted upon by forces on all surfaces, it was decided to use the surface area when evaluating the force per unit area.

Figure 3 illustrates the method used to evaluate the yield value of the mucilages. The important section of the figure is the points where the curves for water and the structural liquid are parallel. The distances between these parallel lines are taken as the yield force of the mucilagenous structure. The values of these forces in terms of surface area for the samples tested are listed in Table I. The single value for the 0.794-cm. sphere is presented for comparison of the value obtained from a different sized sphere.

DISCUSSION

The behavior of the EMY curves for structural fluids agrees with Bingham's theory of an opposing elastic force which resists the downward movement of the sphere. This resisting elastic force increases as the sphere moves downward. The curve initially is linear, followed by a nonlinear section where the force is not directly proportional to displacement. Finally, the downward force is large enough to rupture the structure of the fluid. The structure is instantaneously recoverable, so the downward force upon the sphere is continually resisted by the elastic forces. This is the region of the parallel EMY curves. The distance between the curves at the same voltage is the amount of force required to exceed the yield force. If a fluid possesses a structure, it can be detected and evaluated in this manner. When flow curves of fluids possessing structure are evaluated, it should be recognized that a resisting elastic force is always present in addition to the resisting viscosity forces.

Table II presents a comparison of the Bingham yield values obtained from data collected from the Rising cylinder rheometer (6) with the yield values obtained from EMY curves. The correlation of the yield values obtained by extrapolating low shear data with the EMY yield values supports the surface area dependency of the forces acting on a suspended particle.

The data presented in Table II indicate that the method of Bingham is not applicable to the pseudoplastic tragacanth system and that even though the extrapolation to the stress axis was made from an apparently linear portion of the flow curve, curvature was still present. The discrepancy in the data with the Carbopol-934 mucilages is due to the effect of temperature. The data from the EMY were collected at room temperature (approximately 26°), while those from the Rising cylinder rheometer were collected at 30°

To study the effect of temperature upon the yield value, Carbopol-934 mucilage 0.23% and tragacanth super initial mucilage were studied again in the EMY at 30°(Table III). As was expected, the yield values of the mucilages were less at 30° than at 26°. The yield value of the Carbopol-934 mucilage appeared to agree favorably with the yield value obtained with the Rising cylinder. However, the value for the tragacanth mucilage did not. This mucilage was studied again at 26°, and its yield value at this temperature did not agree with the previous determination. It was noted that the previous determination had been made on freshly prepared mucilage, while the mucilage currently being studied was 1 month old. This indicated that the tragacanth mucilage lost considerable suspending ability in 1 month.

Bingham yield values were obtained for other tragacanth mucilages utilizing data collected from the Rising cylinder rheometer and tabulated previously (6). These same mucilages were now studied in the EMY and found to have little or no yield values. The mucilages had been aging for 6 months. It can be concluded therefore that the structural properties of Carbopol-934 mucilages is relatively permanent, while those of tragacanth mucilages deteriorate rapidly with time.

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