

Figure 4—Scan of derivatized sulfonamides separated on a silica gel TLC plate by development twice in diethyl ether (11 cm). Sulfonamides are: A, sulfathiazole; B, sulfadiazine; C, sulfamerazine; D, sulfadimidine; and E, sulfamethoxazole.

sensitive and specific method utilizing these principles for the development of a tissue residue assay for sulfadiazine is described.

Fluorescamine was used previously as a means for detection of amino acids on TLC plates, but the quantitative aspects were not pursued (4). This report emphasizes the utility of this reagent as a useful analytical tool, especially for residue level determinations of

sulfonamides. Undoubtedly, numerous extensions of this approach to include a broad range of drugs and pesticides can be made.

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Predicting Subjective Spreadability, Viscosity, and Stickiness

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Abstract □ Subjective spreadability, viscosity, and stickiness perceived with the fingers were predicted from fluid mechanics. The correlation coefficients of these predictions were 0.95 for spreadability, 0.95 for viscosity, and 0.90 for stickiness. The two important assumptions in the predictions were that spreadability and viscosity were perceived as shear stress and that stickiness was perceived as time. When the finger geometry was approximated as two parallel plates, the predictions only required rheological data for the Newtonian and non-Newtonian liquids used. While these liquids covered a range of 10^6 in apparent viscosity, large variations in other fluid properties such as density and surface tension were not studied.

Keyphrases □ Spreadability, subjective—predicted from fluid mechanics, equations □ Viscosity, subjective—predicted from fluid mechanics, equations □ Stickiness, subjective—predicted from fluid mechanics, equations □ Liquid texture—predicting subjective spreadability, viscosity, and stickiness

Previous papers on liquid texture presented interesting empirical relationships between subjective attributes and rheological parameters (1-7). For exam-

ple, Stevens and Guirao (2) found for Newtonian liquids that:

$$\left(\frac{\text{subjective}}{\text{viscosity}} \right) \propto \left(\frac{\text{objective}}{\text{viscosity}} \right)^{0.44} \quad (\text{Eq. 1})$$

where the exponent of 0.44 is found empirically. As a second example, empirical curves were found (4, 6, 7) giving the conditions under which fluids of different rheological properties have the same subjective texture. Why these curves have their peculiar shape remained uncertain.

This paper predicts some attributes of liquid texture without introducing empiricism. It depends on two key assumptions: (a) that subjective stickiness is perceived as the time during which the finger is pulled away from the sticky surface, and (b) that subjective spreadability and viscosity are perceived as the shear stress on the fingers. That these assumptions are sensible is easily tested. For example, when water and honey are rubbed between the fingers, the

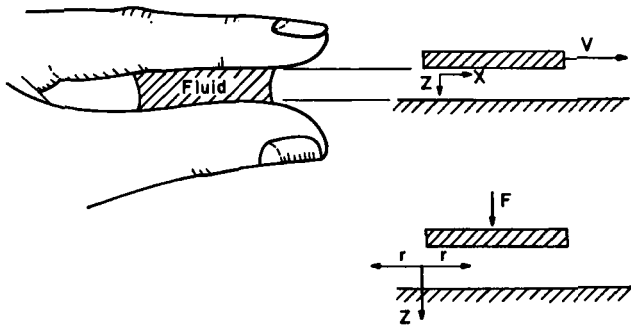


Figure 1—Schematic representation of finger geometry as two parallel plates.

fingers move in an oscillating motion with a constant period and amplitude; the finger velocity varies little with changes in objective liquid viscosity. Since the subjective viscosities of honey and water are very different, the subjective viscosity must be perceived not as velocity but as another quantity such as shear stress. This type of observation will be shown to lead to the successful prediction of liquid texture.

THEORETICAL

Finger Geometry and Fluid Rheology—There were three basic steps in developing predictions of spreadability, viscosity, and stickiness:

1. The finger geometry and fluid rheology were specified.
2. Equations for the thickness of the fluid film on the fingers as a function of time were developed.
3. How this fluid thickness leads to equations for predicting spreadability, viscosity, and stickiness was demonstrated.

In the first step, the actual geometry of the fingers was approximated by two parallel plates (Fig. 1). This approximation is reasonable only when the thickness of the sample is small relative to the radius of the finger. As suggested in Fig. 1, the shear force between the fingers is most easily found using Cartesian coordinates with the origin on one moving finger, but the thickness is most easily calculated in terms of cylindrical coordinates with the origin at the center of the film.

Just as parallel plates were used to approximate the finger geometry, the empirical power law model was assumed to approximate the fluid rheology (8):

$$\tau_{zx} = -m \left(\frac{\partial v_x}{\partial z} \right)^n \quad (\text{Eq. 2})$$

where τ_{zx} is the shear stress on a plane normal to the z direction and caused by motion in the x direction, v_x is the fluid velocity in the x direction, and m and n are rheological constants of this model. For a Newtonian fluid, n is unity and m is the viscosity; for the non-Newtonian fluids used in this work, n was always less than 1. The use of this equation required that the coordinate system be defined so that $(\partial v_x / \partial z)$ was always positive and τ_{zx} was not imaginary. Therefore, the coordinate system had to be redefined every time the velocity was reversed.

Thickness of Fluid Film—The second basic step in developing the desired predictions was to calculate fluid thickness for the approximate geometry and rheology. This problem was solved for Newtonian fluids by Stefan (9), yielding results frequently used in lubrication theory (10). For the power law fluids considered here, the equation of motion in cylindrical coordinates is:

$$\frac{\partial p}{\partial r} = -\frac{\partial \tau_{zr}}{\partial z} = m \frac{\partial}{\partial z} \left(\frac{\partial v_r}{\partial z} \right)^n \quad (\text{Eq. 3})$$

where p is the pressure and τ_{zr} is the stress on a plane normal to the z direction caused by motion in the r direction. The first boundary condition used with Eq. 3 was that the shear stress is zero in the exact center of the film; i.e., that $\partial v_r / \partial z = 0$ when $z = 0$. The second boundary condition was that the velocity at the plates is zero; i.e., that $v_r = 0$ when $z = \pm h/2$, where h is the film thick-

ness between the fingers. Equation 3 was integrated using these conditions:

$$v_r = \left[\frac{1}{m} \frac{\partial p}{\partial r} \right]^{1/n} \frac{n}{n+1} \left[z^{(1/n)+1} - \left(\frac{h}{2} \right)^{(1/n)+1} \right] \quad (\text{Eq. 4})$$

The volumetric flow per unit arc, Q , was defined across a fluid element shaped like a piece of pie:

$$Q = \frac{2 \int_0^{h/2} \int_0^{2\pi} v_r r \, d\theta \, dz}{\int_0^{2\pi} r \, d\theta} = 2 \int_0^{h/2} v_r \, dz \quad (\text{Eq. 5})$$

Therefore, from Eqs. 4 and 5, Q was:

$$Q = 2 \left[\frac{1}{m} \frac{\partial p}{\partial r} \right]^{1/n} \frac{n}{n+1} \int_0^{h/2} \left[z^{(1/n)+1} - \left(\frac{h}{2} \right)^{(1/n)+1} \right] dz \quad (\text{Eq. 6})$$

Then Q was related to the decrease of the fluid thickness by means of a mass balance on the same pie-shaped element already used:

$$-\frac{dh}{dt} = \frac{1}{r} \frac{\partial}{\partial r} (Qr) \quad (\text{Eq. 7})$$

Equations 6 and 7 were next combined and integrated using two more boundary conditions. The first of these was that the pressure is always finite or, in other words, that $p \neq \infty$ when $r = 0$. The second condition was that the pressure must be the atmospheric value p_0 at the edge of the fingers; i.e., $p = p_0$ at $z = \pm h/2$ and $r = R$, where R is the effective radius of the fingers. The result of this integration was:

$$p = p_0 + \frac{m}{n+1} \left(\frac{2n+1}{4n} \right)^n \left(\frac{2}{h} \right)^{2n+1} \left(\frac{dh}{dt} \right)^n [R^{n+1} - r^{n+1}] \quad (\text{Eq. 8})$$

In this integration, dh/dt was assumed to be approximately constant. This pseudo-steady-state approximation took advantage of the fact that steady-state pressure gradients are approached rapidly.

Before Eq. 8 was finally integrated, it was rewritten in terms of the total normal force, F_0 , acting on the plates:

$$F_0 + \pi R^2 p_0 = 2\pi \int_0^R p r \, dr \quad (\text{Eq. 9})$$

Combination of Eqs. 8 and 9 and integration over r yielded:

$$\frac{F_0}{R^{n+3}} \left(\frac{n+3}{2\pi m} \right) \left(\frac{n}{2n+1} \right)^n = \left(\frac{1}{h} \right)^{2n+1} \left(\frac{dh}{dt} \right)^n \quad (\text{Eq. 10})$$

a result similar to that of Parlato (11). Since the total normal force by the fingers was assumed a constant, the n th root of this equation could be integrated over time:

$$h = \frac{1}{\left[\frac{1}{h_0^{(n+1)/n}} + \left(\frac{F_0 n + 3}{R^{n+3} 2\pi m} \right)^{1/n} \frac{n+1}{2n+1} t \right]^{n/(n+1)}} \quad (\text{Eq. 11})$$

where h_0 is the initial film thickness at zero time. This equation shows how the thickness of the fluid film varies with time, finger geometry, and fluid rheology. It formed the basis for the predictions of subjective properties given in the next section.

Subjective Predictions—Spreadability—The third step in this development was the prediction of the subjective attributes. First, spreadability was assumed to be proportional to the reciprocal of the shear stress:

$$\left(\text{subjective spreadability} \right) \propto \frac{1}{\tau_{\text{spread}}} \quad (\text{Eq. 12})$$

For a thin film, combination of Eqs. 2 and 12 gave:

$$\left(\text{subjective spreadability} \right) \propto \frac{1}{m} \left(\frac{h}{V_{\text{spread}}} \right)^n \quad (\text{Eq. 13})$$

where V_{spread} is the steady velocity of the finger used in assessing

spreadability. This result was combined with Eq. 11 to give:

$$\left(\begin{array}{c} \text{subjective} \\ \text{spreadability} \end{array} \right) \propto \frac{1}{mV_{\text{spread}}^n} \left[\frac{1}{h_0^{(n+1)/n}} + \left(\frac{F_0}{R^{n+3}} \frac{n+3}{2\pi m} \right)^{1/n} \times \frac{n+1}{2n+1} t_{\text{spread}} \right]^{-n^2/(n+1)} \quad (\text{Eq. 14})$$

where t_{spread} is the average assessment time for spreading. Since all quantities on the right-hand side of this equation were measured by independent experiments, Eq. 14 provided a means of calculating spreadability. A plot of experimentally measured subjective spreadability versus the right-hand side of Eq. 14 should be linear.

Viscosity—Viscosity was assumed to be perceived as the shear stress, τ_{visco} , exerted on the finger:

$$\left(\begin{array}{c} \text{subjective} \\ \text{viscosity} \end{array} \right) \propto \tau_{\text{visco}} = m \left(\frac{V_{\text{visco}}}{h} \right)^n \quad (\text{Eq. 15})$$

where V_{visco} is the average finger velocity used on the thin fluid film. In fact, viscosity is assessed by rubbing the fingers with an oscillating motion, but the exact analysis of this motion is very elaborate (12). Combination of Eqs. 11 and 15 gave:

$$\left(\begin{array}{c} \text{subjective} \\ \text{viscosity} \end{array} \right) \propto m(V_{\text{visco}})^n \left[\frac{1}{h_0^{(n+1)/n}} + \left(\frac{F_0}{R^{n+3}} \frac{n+3}{2\pi m} \right)^{1/n} \times \frac{n+1}{2n+1} t_{\text{visco}} \right]^{n^2/(n+1)} \quad (\text{Eq. 16})$$

where t_{visco} is the assessment time for viscosity. All quantities on the right-hand side of Eq. 16 were determined experimentally. As a result, a plot of experimentally determined subjective viscosity versus the right-hand side of Eq. 16 should be linear.

For two special cases, the subjective viscosity could be predicted in simpler ways. First, for Newtonian fluids for which the initial thickness was large, $n = 1$, $m = \mu$, and $h \ll h_0$. Under these conditions, Eq. 16 is reduced to:

$$\left(\begin{array}{c} \text{subjective} \\ \text{viscosity} \end{array} \right) \propto \mu^{1/2} \left[V_{\text{visco}} \left(\frac{4F_0 t_{\text{visco}}}{3\pi R^4} \right)^{1/2} \right] \quad (\text{Eq. 17})$$

All quantities in brackets are characteristic of the assessment but experimentally independent of the fluid being judged. Thus, if subjective viscosity was, in fact, perceived as shear stress, a plot of the logarithm of subjective spreadability versus the logarithm of objective viscosity should have a slope of one-half.

The second special case for predicting subjective viscosity occurred when the film was mechanically prevented from thinning by means of a small sled holding the finger a constant distance from the surface (13). In this case, Eq. 15 assumed a very simple form for Newtonian fluids:

$$\left(\begin{array}{c} \text{subjective} \\ \text{viscosity} \end{array} \right) \propto \tau_{\text{visco}} = \mu \left[\frac{V_{\text{visco}}}{h} \right] \quad (\text{Eq. 18})$$

where h is now a constant of the small sled. The quantity in brackets is again characteristic of the assessment but independent of the fluid being judged. If subjective viscosity was truly perceived as shear stress, a plot of the logarithm of subjective viscosity assessed at constant film thickness versus the logarithm of objective viscosity should have a slope of unity.

Stickiness—Unlike spreadability and viscosity, which were assessed with a shearing motion, stickiness was assessed by a motion normal to the surface. First the finger was pressed against the sample being judged, and then the finger was pulled away. While the fluid mechanics in this situation were less well defined than for the previous two cases, the thickness of the film during this assessment can be approximately calculated from Eq. 11.

Stickiness was assumed to be perceived as the time during which the finger is pulled away from the sticky surface. This time varied inversely with the average velocity normal to the surface of the moving finger, dh/dt :

$$\left(\begin{array}{c} \text{predicted} \\ \text{stickiness} \end{array} \right) \propto \frac{H}{dh/dt} \quad (\text{Eq. 19})$$

where H is the distance at which the finger separates from the fluid. In general, H was a function of the fluid being tested. How-

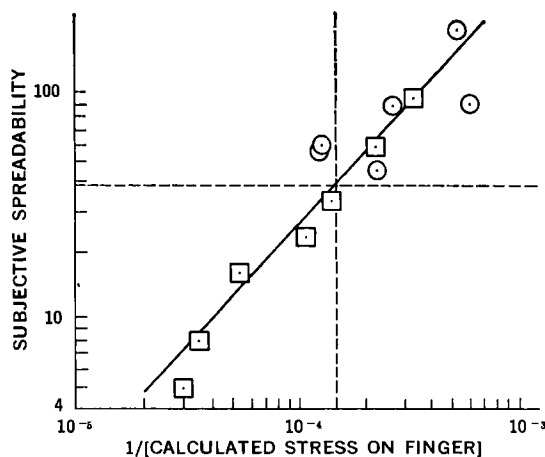


Figure 2—Subjective spreadability versus [shear stress]⁻¹. The best line through the data has a slope of 1.05 ± 0.05, compared with a predicted value of 1.00. The circles and squares are Newtonian and non-Newtonian fluids, respectively.

ever, because the surface tension had approximately the same value for all of the fluids used, H was approximately a constant here.

The velocity dh/dt can be calculated from Eq. 11 and combined with Eq. 19 to yield:

$$\left(\begin{array}{c} \text{subjective} \\ \text{stickiness} \end{array} \right) \propto \frac{H(2n+1)}{n} \times \frac{\left[\frac{1}{h_1^{(n+1)/n}} - \frac{n+1}{2n+1} \left(\frac{F_1}{R^{n+3}} \frac{n+3}{2\pi m} \right)^{1/n} t_{\text{stick}} \right]^{(1+2n)/(1+n)}}{\left(\frac{F_3}{R^{n+3}} \frac{n+3}{2\pi m} \right)^{1/n}} \quad (\text{Eq. 20})$$

where h_1 is the minimum film thickness after squeezing the film, F_1 is the normal force developed in pulling the finger upward, and t_{stick} is an average reference time. All quantities on the right-hand side of Eq. 20 were determined experimentally except for h_1 , which was calculated from Eq. 11. Thus, a plot of experimentally measured subjective stickiness versus the right-hand side of Eq. 20 should be a straight line.

EXPERIMENTAL

Objective Measurements—The Newtonian fluids used in this work were silicone oils¹ ranging in viscosity from 2.6 to 85,000 cps. The non-Newtonian fluids included aqueous solutions of hydroxypropyl methylcellulose and aqueous solutions of polyacrylamide. Three grades of hydroxypropyl methylcellulose² were used as 2 wt. % solutions in water. The polyacrylamide solutions were prepared by polymerization of 2, 4, and 8% monomer in water. Polymerization was initiated with persulfate-bisulfite and continued at 60° for about 1 hr. Viscosities of the Newtonian fluids were measured with capillary viscometers³, calibrated with Newtonian viscosity standards⁴. Rheological parameters of the non-Newtonian fluids were measured with a cone-and-plate viscometer⁵.

In addition to these rheological properties, the predictions of spreadability, viscosity, and stickiness depended on various characteristics of the finger and its motion. Three of these characteristics were similar for all three subjective attributes: the average radius of the finger, R ; the force used in thinning the film, F_0 ; and the initial film thickness, h_0 . The average radius of the finger for 20 people was 0.75 cm, consistent with the measurements of Schaeffer and Chakravarti (14) who used a plate of 0.73 cm as a model of the second fingertip in the design of a commercial instru-

¹ Union Carbide.

² Methocel HG, labeled as 400, 8000, and 15,000 cps; Dow Chemical Co.

³ Ubbelohde type, Fisher Scientific Co.

⁴ Cannon Instrument Co., State College, Pa.

⁵ Rheomat 15, Olkon Corp.

Table I—Spreadability for Eight Newtonian and Six Non-Newtonian Fluids^a

Fluid	<i>m</i>	<i>n</i>	Measured <i>h</i> ₀	Measured <i>V</i> _{spread}	Reciprocal Calculated Stress ^b	Subjective Spreadability
Water, 1 cps	0.01	1.0	0.013	7.4	12.3 ^c	105.
Silicone oil, 20 cps	0.20	1.0	0.018	6.2	3.3	97.
Silicone oil, 70 cps	0.70	1.0	0.040	4.9	2.2	58.
Silicone oil, 936 cps	9.36	1.0	0.034	2.2	1.3 _s	33.
Silicone oil, 1770 cps	17.70	1.0	0.046	2.0	1.0 _r	23.
Silicone oil, 8450 cps	84.50	1.0	0.055	1.8 _z	0.5 _i	16.
Silicone oil, 23,300 cps	233.0	1.0	0.072	1.6 _r	0.35	7.9
Silicone oil, 85,000 cps	850.0	1.0	0.068	0.97	0.30	4.9
Polyacrylamide, 2%	0.13	0.93	0.031	7.8	5.4	190.
Polyacrylamide, 5%	28.	0.52	0.056	4.8	6.0	90.
Polyacrylamide, 8%	390.	0.47	0.066	6.1	1.2 _a	55.
Hydroxypropyl methylcellulose, 400 cps, 1.5%	3.4	0.79	0.057	7.3	2.7	88.
Hydroxypropyl methylcellulose, 8000 cps, 2%	93.	0.62	0.084	6.4	1.2 _a	58.
Hydroxypropyl methylcellulose, 15,000 cps, 2%	630.	0.32	0.066	5.0	2.2	46.

^a Units used here are as follows: *m*, dynes sec² cm⁻²; *h*₀, cm; *V*, cm sec⁻¹; and calculated spreadability, 10⁻⁴ cm² dyne⁻¹. Other quantities are dimensionless. ^b These calculations involve three additional experimentally measured quantities: the average normal force, *F*₀, of 89,000 dynes; the average finger radius, *R*, of 0.75 cm; and the average assessment time, *t*_{spread}, of 10 sec. ^c Not included in the regression analysis.

ment. The normal force for thinning the film was found by placing different samples on the pan of a magnetic balance and then by touching the fluids in an imitation of the subjective assessments. Each of 20 people used the same force for all fluids, independent of the fluid's viscosity. This force was about 89,000 ± 5000 dynes.

The initial thickness of the sample, *h*₀, was measured directly in the case of spreadability as the mass of fluid adhering to the finger divided by the finger area. These values did vary with viscosity and are reported in the *Results* section. The same values were also used in calculations of viscosity and stickiness but had little effect on the calculations. Indeed, assuming that *h*₀ always equaled 0.1 cm gave equivalent results in these two cases.

The basic equations for predicting spreadability, viscosity, and stickiness also contained characteristics of finger motion, which were specific for the attribute being studied. For spreadability, these characteristics were the velocity of the finger, *V*_{spread}, and the time of spreading, *t*_{spread}, both of which were measured with a stopwatch during the subjective experiments. The velocity varied with viscosity and is reported below, but the time of spreading was a constant for each subject and had an average value of 10 sec. For viscosity, the specific characteristics were the average velocity of finger motion, *V*_{visco}, and the time of assessment, *t*_{visco}. These quantities, also measured during the subjective experiments, were both constant, independent of viscosity. The velocity had a period of 1.0 ± 0.2 sec and an amplitude of 0.5 ± 0.1 cm. The time for the assessment of viscosity was found to be 5 ± 1 sec.

For stickiness, the specific characteristics necessary for the calculations were the force used in pulling up the finger, the time of squeezing the fluid, and the time of pulling the finger. The pulling force was measured with a balance (14). The time for squeezing, measured with a balance and a stopwatch during some of the subjective experiments, was a constant 3.0 ± 0.2 sec. The time of pulling was measured as 0.1 sec, but this measurement was approximate.

Subjective Measurements—For each textural characteristic, panels of between 15 and 24 members of both sexes, ranging in age from 20 to 50 years and not trained prior to the present work, were asked in written instructions (14) to assess the different fluid samples relative to the first sample. These samples were presented in random order on a plastic plate at room temperature. For spreadability, observers spread the samples along the plate with their index finger; for viscosity, observers often preferred to rub the samples between their fingers and were permitted to do so; for stickiness, observers touched the sample and then pulled their fingers away.

Whenever necessary, observers were allowed to go back to the standard for comparison. A judgment of zero was not accepted for any property; in that case, the concept of ratio scaling was clarified, and use of fractional numbers (1/10, 1/100, etc.) was encouraged. The subjective data were analyzed with linear regression analysis after a logarithmic transformation (15).

RESULTS

Spreadability—The agreement of the experimental and predicted values of the subjective assessments is clearest if the three attributes of spreadability, viscosity, and stickiness are discussed sequentially. The raw data for spreadability are shown in Table I. The first three columns give the fluid and its rheological parameters in terms of the power law model in Eq. 2. The next two columns give the initial thickness, *h*₀, and the spreading velocity, *V*_{spread}, both measured during the subjective assessments. The sixth column gives the reciprocal of the stress calculated from Eq. 14, using experimental quantities shown in the table. The final column gives the subjective spreadability measured by ratio scaling. The value for water deviates considerably from the trend shown by the other fluids; it probably lies outside the range of perception and was discarded when estimating the regression line.

The theory for spreadability predicts that a plot of the logarithm of subjective spreadability versus the logarithm of the right-hand side of Eq. 14 should be a straight line of slope unity. This prediction is in excellent agreement with the experimental slope of 1.05 ± 0.05 (Fig. 2). Phrased in other terms, the correlation coefficient between subjective spreadability and the reciprocal of the shear stress is 0.95. This correlation is impressive.

Equation 14 also predicts that two Newtonian fluids of different viscosities will never have the same subjective spreadability. In this case, *n* is always unity, so different values of *m* = μ imply dif-

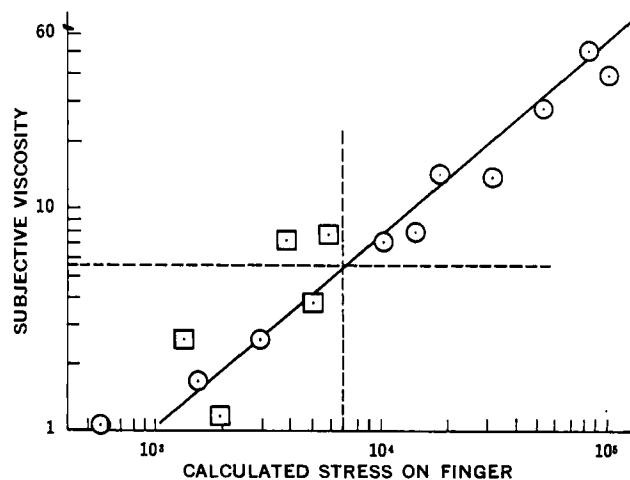


Figure 3—Subjective viscosity versus shear stress. The best line through the data has a slope of 0.86 ± 0.02, compared with a predicted value of 1.00. The circles and squares are Newtonian and non-Newtonian fluids, respectively.

Table II—Apparent Viscosity for 10 Newtonian and Six Non-Newtonian Fluids^a

Fluid	<i>m</i>	<i>n</i>	<i>h</i> ₀	Predicted Viscosity ^b	Subjective Viscosity
Silicone oil, 2.6 cps	0.026	1.0	0.015	0.56	1.06
Silicone oil, 20 cps	0.20	1.0	0.018	1.5	1.70
Silicone oil, 70 cps	0.70	1.0	0.040	2.9	2.6
Silicone oil, 936 cps	9.36	1.0	0.034	11.	7.2
Silicone oil, 1770 cps	17.7	1.0	0.046	15.	7.9
Silicone oil, 2805 cps	28.05	1.0	0.049	18.	14.2
Silicone oil, 8450 cps	84.50	1.0	0.055	32.	13.6
Silicone oil, 23,300 cps	233.0	1.0	0.072	54.	28.
Silicone oil, 51,500 cps	515.0	1.0	0.070	85.	51.
Silicone oil, 85,000 cps	850.0	1.0	0.068	110.	39.
Polyacrylamide, 2%	0.13	0.93	0.031	0.79	0.3 ₁
Polyacrylamide, 5%	28.	0.52	0.056	1.3	2.6
Polyacrylamide, 8%	390.	0.47	0.066	5.9	7.7
Hydroxypropyl methylcellulose, 400 cps, 1.5%	3.4	0.79	0.057	1.9	1.17
Hydroxypropyl methylcellulose, 8000 cps, 2%	93.	0.62	0.084	5.1	3.8
Hydroxypropyl methylcellulose, 15,000 cps, 2%	630.	0.32	0.066	3.9	7.4

^a Units used here are as follows: *m*, dynes secⁿ cm⁻²; predicted viscosities, 10⁻³ dynes cm⁻²; and *h*₀, cm. Other quantities are dimensionless. ^b These predictions use four additional experimentally measured quantities: the average finger radius, *R*, of 0.75 cm; the average normal force, *F*₀, of 89,000 dynes; the average velocity, *V*_{visco}, of 3.1 cm sec⁻¹; and the average assessment time of 5 sec.

ferent spreadabilities. On the other hand, groups of non-Newtonian fluids can have the same spreadability when *m* and *n* differ. The only requirement is that the combination of *m* and *n* given by Eq. 14 results in the same predicted spreadability.

The results in Table I and Fig. 2 support this prediction. For example, silicone oil (936 cps) and silicone oil (1770 cps) are perceived subjectively as 33.0 and 23.0, respectively. However, the data confirm that a Newtonian fluid can show the same spreadability as a variety of non-Newtonian fluids with very different values of *m* and *n*. For example, silicone oil (70 cps), polyacrylamide (8%), and hydroxypropyl methylcellulose (8000 cps, 2%) all have about the same spreadability (58.0, 55.0, and 58.0, respectively), even though their rheological parameters are very different.

Viscosity—The data for subjective and predicted viscosity are shown in Table II. The first three columns give the rheological properties of the fluids in terms of Eq. 2. The initial film thickness, *h*₀, in the fourth column is not critical in the calculations; changes in these values by a factor of 2 have little effect on the results. The fifth column gives the predicted viscosity calculated from Eq. 16, using the values given in this table. The final column reports the subjective viscosity.

The theory predicts that a plot of the logarithm of subjective viscosity versus the logarithm of the right-hand side of Eq. 16 should be linear with a slope of 1. This predicted slope is in good

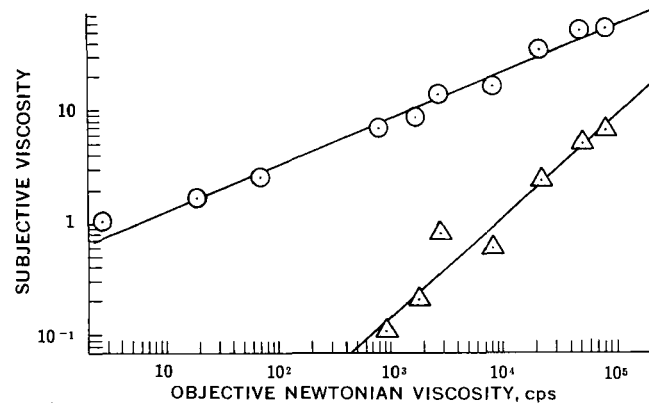


Figure 4—Subjective viscosity versus objective Newtonian viscosity. The circles are values obtained when the thickness of fluid on the fingers varies during the assessments. The best line through these data has a slope of 0.40 ± 0.01 , compared with 0.50 predicted by Eq. 17. The triangles represent assessments at constant fluid thickness; the best line through these values has a slope of 0.89 ± 0.06 , compared with 1.00 predicted by Eq. 18.

agreement with the experimental value of 0.86 ± 0.02 (Fig. 3). The correlation coefficient between subjective viscosity and the calculated stress on the finger is 0.95. The agreement is not quite as close as that found for spreadability. However, in the derivation of the theory for viscosity, the major assumption was made that the periodic motion of the fingers can be approximated as a steady motion between parallel plates. In view of this approximation, the predictions of the theory are very good.

Other theoretical predictions for Newtonian fluids are tested in Fig. 4. The circles in this plot represent the logarithm of subjective viscosity plotted versus the logarithm of objective viscosity of the Newtonian fluid. The slope of the line drawn through these data is 0.40 ± 0.01 , in good agreement both with other experimental studies of subjective viscosity (3) and with the value of 0.50 predicted by Eq. 17. Since the prediction requires only a measurement of Newtonian viscosity, additional properties like finger area and assessment time are constant and need not be measured experimentally.

These results and the others in this paper were unaffected by the temperature of the samples. For example, subjective Newtonian viscosity evaluated at skin temperature of 32° leads to an exponent of 0.41. This insensitivity is a consequence of ratio scaling. While viscosity changes significantly with temperature, the changes are similar percentages for all fluids used. Thus, the relative subjective viscosity measured by ratio scaling does not depend strongly on temperature.

The triangles in Fig. 4 represent the logarithm of subjective viscosity assessed at constant film thickness and plotted versus the

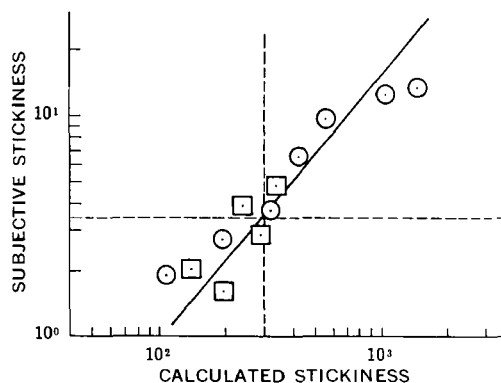


Figure 5—Subjective stickiness versus stickiness calculated from Eq. 20. The best line through the data has a slope of 1.12 ± 0.08 , compared with a predicted value of 1.00. The circles and squares are Newtonian and non-Newtonian fluids, respectively.

Table III—Stickiness for Six Newtonian and Six Non-Newtonian Fluids*

Fluid	<i>m</i>	<i>n</i>	<i>F</i> ₁	Calculated <i>h</i> ₁ ^b	Stickiness from Eq. 20 ^c	Subjective Stickiness
Silicone oil, 936 cps	9.36	1.0	1.3	0.94	1.0 ₇	1.8 ₇
Silicone oil, 1770 cps	17.70	1.0	1.7	0.68	1.9 ₂	2.7
Silicone oil, 2805 cps	28.05	1.0	1.9	0.86	3.2	3.8
Silicone oil, 8450 cps	84.50	1.0	2.1	1.09	4.2	6.6
Silicone oil, 23,300 cps	233.0	1.0	2.7	1.29	5.7	9.8
Silicone oil, 51,500 cps	515.0	1.0	2.8	1.35	10.7	12.5
Silicone oil, 85,000 cps	850.0	1.0	3.4	1.35	15.0	13.2
Polyacrylamide, 2%	0.13	0.93	1.2	0.15	0.85	0.2 ₇
Polyacrylamide, 5%	28.	0.52	1.6	0.42	1.3 ₉	2.0
Polyacrylamide, 8%	390.	0.47	1.4	1.30	3.4	4.7
Hydroxypropyl methylcellulose, 400 cps, 1.5%	3.4	0.79	1.7	0.30	1.9 ₅	1.6 ₂
Hydroxypropyl methylcellulose, 8000 cps, 2%	93.	0.62	1.8	0.78	2.9	2.9
Hydroxypropyl methylcellulose, 15,000 cps, 2%	630.	0.32	2.1	1.30	2.4	3.9

* Units used here are as follows: *m*, dynes sec² cm⁻²; pulling force, *F*₁, 10⁶ dynes; calculated *h*₁, 10⁻² cm; and calculated stickiness, 10² sec cm⁻¹. Other quantities are dimensionless. ^b These predictions use four additional experimentally determined quantities: the average finger radius, *R*, of 0.75 cm; the average force thinning the film, *F*₀, of 89,000 dynes; the initial film thickness, *h*₀, given in Tables I and II; and the average time thinning the film of 3 sec. ^c These calculations use one additional experimentally estimated quantity: the average time for pulling up the finger, *t*_{stick}, of 0.1 sec.

logarithm of objective viscosity. These data were obtained by attaching to the finger a small sled with 0.06-cm runners, so that the finger touched the fluid but did not thin the fluid film. The best line through these data has a slope of 0.89 ± 0.06, in good agreement with the value of 1.00 predicted from Eq. 18. This slope is also consistent with earlier experiments showing that perceived force varies linearly with objective applied force (1). Both this result and the previous one illustrate how fluid mechanics, exemplified here by film thinning, influences the subjective perceptions.

Stickiness—The data for subjective and predicted stickiness are shown in Table III. The first three columns again give the fluid and its rheological properties. The final column gives the subjective stickiness as determined by ratio scaling.

The remaining data are connected with the calculations, which are more involved in this case than in spreadability and viscosity. The calculation has two main steps. First, one must find the film thickness, *h*₁, at which the film is thinnest. Because *h*₁ was not accurately measured experimentally, it must be calculated from Eq. 11. The key variable in this calculation is the time that the film is thinned by squeezing, which was found by experiment to be 3 sec. The second step is the calculation in Eq. 20, which depends on the minimum film thickness, *h*₁, calculated in the first step; the pulling force, *F*₁, measured experimentally; and the average time, *t*_{stick}, for pulling the finger upward. This time was estimated as 0.1 sec, but this estimation is not definitive.

The theory culminating in Eq. 20 predicts that a plot of the logarithm of subjective stickiness versus the logarithm of the right-hand side of Eq. 20 should have a slope of 1. This predicted slope is in good agreement with the experimentally determined slope of 1.12 ± 0.08 (Fig. 5). However, the agreement is not as good as that found in the two previous cases: the correlation coefficient between subjective and predicted stickiness is only 0.90. This poorer agreement is probably a consequence of the much more involved calculations.

Conclusions and Limitations—The picture emerging from this study has a beguiling symmetry. For attributes assessed by a shearing motion, such as spreadability and viscosity, the perception is of shear force with (approximately) constant velocity. For attributes assessed by a normal motion, like stickiness, the perception is proportional to time or velocity with (approximately) constant force. Calculations based on this picture give correlation coefficients of 0.90 or better between subjective and predicted assessments. These calculations are most definitive for Newtonian liquids, where no additional properties need be measured. They are also successful for spreadability, where the additional parameters involved are easily measured. The calculations are least successful for stickiness, where they are most complex.

However, the results given in this paper are limited by the fact that only the apparent viscosity of the fluids varies widely. This single variable is doubtless partially responsible for the well-defined conclusions that were reached. The effect of large changes in

other physical properties may not be minor. For example, three physical properties that would alter the results are fluid elasticity, fluid finger wetting, and fluid thermal conductivity. The first of these properties, which requires a more complex rheological model than that in Eq. 3, is probably more important for subjective "slipperiness" than for the three attributes involved here (15). When studying elastic fluids, observers using ratio scaling frequently gave a value of zero to any nonelastic fluid, regardless of its viscosity.

Wetting between the fluid and the finger will strongly affect the total amount of fluid adhering to the finger and will change *h*₀ used in calculating both spreadability and viscosity. It also will affect *H*, the distance at which the finger separates from the fluid in the assessment of stickiness. Changes in fluid thermal conductivity are probably most important in the colloidal systems used in cosmetics, where the oil-in-water emulsion changes rapidly into a water-in-oil emulsion. This emulsion "break" causes a sudden 300% change in the heat lost by the finger. These effects should be much easier to predict than those of elasticity.

Because of these limitations, the results in this paper are a first step rather than an exhaustive picture. They allow the *a priori* prediction of some empirical exponents in Stevens' law. They give a firmer basis to the universal curves of equivalent texture (5-7). They suggest a rationale for ingredient substitutions and may aid in planning test panels, but they are certainly no substitute for these panels. Nevertheless, the results provide an intriguing indication that consumer reactions may be strongly influenced by physical restraints such as fluid mechanics.

NOMENCLATURE

- F*₀ = force used in thinning the film
- F*₁ = normal force developed in pulling the finger upward during assessment of stickiness
- h* = thickness of the fluid sample at any time *t*
- h*₀ = initial thickness of the fluid sample
- h*₁ = minimum film thickness after squeezing during assessment of stickiness
- H* = distance at which the finger separates from the fluid in assessment of stickiness
- m, n* = consistency and flow index in the power law model for non-Newtonian fluids
- P* = pressure
- P*₀ = atmospheric pressure
- Q* = volumetric flow per unit arc
- R* = radius of the finger
- t* = time
- t*_{spread}, *t*_{visco} = times of assessments of spreadability, viscosity, and stickiness, respectively
- t*_{stick}
- v*_x = velocity of flow in the *x* direction (Cartesian coordinates)

v_r = velocity of flow in the r direction (cylindrical coordinates)
 $V_{\text{spread}}, V_{\text{visco}}$ = average velocity with which the finger moves in assessment of spreadability and viscosity
 μ = viscosity of Newtonian fluids
 τ_{zx}, τ_{zr} = components of shear stress
 $\tau_{\text{spread}}, \tau_{\text{visco}}$ = stress exerted by the fluid on the finger during assessment of spreadability and apparent viscosity, respectively

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Electronic Spectra and Electronic Structures of Some Antimicrobials Derived from Proflavine

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Abstract □ The shifts in the absorption and fluorescence spectra of 3-aminoacridine, proflavine, acridine orange, and acridine yellow were employed to show that the singly charged cations, the predominant species at biological pH, exist in the ground state in the amino form. In the lowest excited singlet state, however, the monocations of the diaminoacridines have the imino structure, a conclusion supported by the relative ground- and excited-state pKa values of the reactions of the monocation with H⁺. The ground-state amino structure has its positive charge concentrated at the heterocyclic nitrogen atom, a fact that is of primary importance in determining the geometry of binding to DNA.

Keyphrases □ 3,6-Diaminoacridine derivatives—electronic spectra and electronic structures □ Proflavine derivatives—electronic spectra and electronic structures □ Antimicrobials—3,6-diaminoacridine derivatives, electronic spectra and electronic structures □ Electronic spectra and structure—diaminoacridine dyes, dependence upon solvent properties and state of protonation □ DNA—interaction with diaminoacridine dyes, electronic spectra and structure of dyes

Several dyes (acridine orange and acridine yellow) derived from proflavine (3,6-diaminoacridine) are employed as bacteriostatic agents, biological stains, and spectroscopic probes of the interactions of nucleic acids with small molecules (1). These substances are well known for their mutagenic effects arising from their interactions with nucleic acids (2). The singly charged cations, which are the prevalent proto-

tropic species, at biological pH derived from proflavine (3,6-diaminoacridine), acridine orange [3,6-bis(dimethylamino)acridine], and acridine yellow (2,7-dimethyl-3,6-diaminoacridine) have been employed extensively in binding studies with nucleic acids (3). These dyes exhibit electronic absorption and fluorescence spectral changes upon binding to DNA.

The interactions of the diaminoacridines with DNA are generally believed to entail electrostatic association of the site of positive charge, in the singly protonated dye molecule, with a negatively charged phosphate ester linkage of the nucleic acid "backbone." In the case of proflavine, it has been shown that the remainder of the dye molecule is inserted between two base pairs of the double helix (or between individual bases in single-stranded nucleic acids), oriented toward the center of the helix and stabilized by hydrophobic interaction with the helix (2). There is, however, some disagreement as to whether the positive charge of the singly protonated diaminoacridine cations is predominately concentrated at the heterocyclic nitrogen atom of the acridine ring (the site of protonation) or at one of the amino nitrogen atoms. This argument arises from the possibility of writing the valence bond structures of the singly protonated cations of proflavine in either of two ways (I and II).