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Keyphrases

Phenyl ethers—synthesis
Antibacterial activity of phenyl pyridyl ethers
Antifungal activity of phenyl pyridyl ethers
Antimalarial activity of phenyl pyridyl ethers
NMR spectrometry
IR spectrometry–structure
Microanalysis

Analog Computer Simulation of Rheological Systems I
Pseudoplastic Flow

By GERALD J. YAKATAN and OSCAR E. ARAUJO

A method for the quantitative characterization of pseudoplastic systems using the analog computer was reported. Three parameters were obtained (one of which can be maintained constant for a given system) which completely describe the shape of rheograms for various CMC mucilages. The method developed can be carried out rapidly, the computer program is relatively simple, and the results should provide an easy means of communication among rheologists desiring to accurately compare experimental data on pseudoplastic systems.

THE IMPORTANCE of pseudoplastic flow in pharmaceutical systems is apparent when one considers that most hydrocolloids and dilute suspensions exhibit this rheological pattern. A large number of pharmaceutical emulsions and semisolid preparations also behave as pseudoplastic systems.

The quantitative characterization of pseudoplasticity has been a difficult problem for the rheologist. The application of an empirical exponential equation involving the use of a log-log plot has been commonly accepted (1–3). However, the use of this equation has been questioned by several workers (4).

Other investigators have proposed various equations with a theoretical basis, but the involved calculations necessary to obtain the constant described considerably reduced their practical value (5–7).

In 1961 Shangraw *et al.* (8) proposed another equation in an attempt to provide a much better representation of non-Newtonian systems. The equation is:

$$F = f + \eta_\alpha S - b_\nu e^{-aS} \qquad \text{(Eq. 1)}$$

where F is the shearing stress, S is the rate of shear, and f, η_α, a, and b_ν are constants characteristic of a particular system.

The problems involved in adequately characterizing pseudoplastic flow systems seemed to offer a challenging area of research. The concept of developing an equation with a minimum number of parameters which would completely characterize all pseudoplastic systems was an interesting one. It was also felt that the analog computer would be of great assistance in solving these problems.

A typical rheogram of a pseudoplastic substance appeared to be composed of a "first-order" and a "zero-order" segment. Consequently, a general equation combining the integrated expressions for a zero-order and a first-order process would be (9):

$$y = ax + b(1 - e^{-cx}) \qquad \text{(Eq. 2)}$$

where y and x are variables for the particular system and a, b, and c are constants for the system.

For a specific rheological system, Eq. 2 becomes:

$$F = aS + b(1 - e^{-cS}) \qquad \text{(Eq. 3)}$$

where F is the shearing stress, S is the rate of shear, and a, b, and c are constants. For purposes of computer programming, F was made directly proportional to voltage and S directly proportional to time, and Eq. 3 becomes:

$$V = at + b(1 - e^{-ct}) \qquad \text{(Eq. 4)}$$

EXPERIMENTAL

The analog computer is rapidly becoming an extremely important tool in aiding the solution of complex scientific and engineering problems. In most modern computers, the continuous variables are d.c. voltages. The electronic analog computer makes possible the building of an electrical system in which d.c. voltages will vary with time in a manner similar to the variable of interest in the actual system under study.

Received May 1, 1967, from the Department of Pharmacy, College of Pharmacy, University of Florida, Gainesville, FL 32601
Accepted for publication September 12, 1967.
The authors are indebted to D. J. Weber for his suggestions and encouragement.
This investigation was supported in part by predoctoral fellowship 5-FI-GM-29,944-02 awarded to G. J. Yakatan from the National Institute of General Medical Sciences, U. S. Public Health Service, Bethesda, Md.

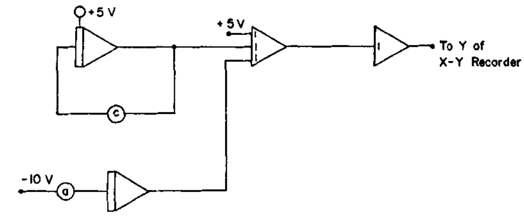

Fig. 1—Analog computer program for simulation of pseudoplastic flow systems.

The analog computer offers a number of distinct advantages for its utilization in the simulation of physical systems. The simple turn of a knob feeds in design parameters. The computer provides an instant-by-instant dynamic picture of each change in a parameter, and each change can be visually compared with any other. Above all, the computer offers simplicity, rapidity, and accuracy in operation.

The present study made use of the Pace TR-10 analog computer[1] and the output from the computer was fed into a Moseley Autograf model 2D-2 X-Y recorder[2] on which the curves were recorded.

The program used to simulate Eq. 4 is shown in Fig. 1. Variable potentiometer settings were used for the parameters a and c. The value of b was maintained constant at +5 v. throughout the study. Plots of shearing stress against rate of shear for pseudoplastic systems pass through the origin. The corresponding computer plot represented by Eq. 4 will also pass through the origin since at $t = 0, v = 0$. Equation 4 was now used to simulate pseudoplastic flow systems by varying two parameters, a and c.

Assuming that pseudoplastic rheograms, obtained by plotting shearing stress *versus* rate of shear, are composed of first-order and zero-order segments, it was deemed advisable to vary one of the two available parameters while holding the other constant. This would show the separate effect of each parameter on the shape of the pseudoplastic curves. The results of this study are shown in Figs. 2 and 3. As expected, the effect of each parameter cannot be separated entirely over the range of values chosen. Nevertheless, an extremely good indication of the effect of varying each parameters was obtained. From these data it seemed probable that by judiciously varying the parameters a and c, rheograms could be drawn which simulate pseudoplastic curves obtained from real systems. To test this theory it was decided to obtain actual experimental data on CMC mucilages known to exhibit pseudoplastic flow.

The rheological measurements were carried out on a Stormer viscosimeter. A weight hanger with various slotted weights provided the shearing stress in Gm. The rate of shear was reported in r.p.m. The CMC mucilages were allowed to equilibrate for 6 hr. after preparation, before any measurements were made. The rheological data, obtained at $20 \pm 0.1°$, are given in Table I.

Figure 4 shows the plots of the experimental points for the various mucilages and the computer curves which were drawn to fit these points. The values of a and c used to draw the simulated computer curves are listed in Table II, along with the values of a and c for the real systems corrected for scaling factors used by the computer. The values of these parameters were determined in the following manner.

A—The experimentally obtained curves, in Gm. *versus* r.p.m., were plotted on graph paper of the same size as that used to draw Figs. 2 and 3.

B—The plot of the experimentally determined points was superimposed on Fig. 2 to roughly estimate the value of c. This procedure was repeated using Fig. 3 to approximate the value of a.

C—These approximate values of a and c were then fed into the computer by adjusting the appropriate potentiometers, and the resulting curve was drawn by the computer on the graph paper containing the experimental points. The recorder was set so that 1 v. = 1 in. and 1 sec. = 1 in. of chart paper.

D—The first curve drawn by the computer never exactly fits the data. However, from this first approximation, changes were made in the values of a and c until a good fit was obtained. This adjustment was always accomplished within 10 min.

E—Now values of a, b, and c are simply read off the potentiometer settings. These values are the parameters of Eq. 4 and consequently must be corrected to the parameters of Eq. 3, which describes the experimental system.

To correct c, the following equation should be used:

$$c_{\text{corr.}} = P \times \frac{M}{R} \qquad \text{(Eq. 5)}$$

where P is the potentiometer setting c in Fig. 1, M is actual machine time at R r.p.m., *i.e.*, if it takes the computer 1 sec. to move 50 r.p.m. on the abscissa then $M/R = 1/50$. To correct a, the following equation should be used:

$$a_{\text{corr.}} = P' \times \frac{k}{k'} \qquad \text{(Eq. 6)}$$

where P' is the potentiometer setting a in Fig. 1, k is the proportionality constant relating F to V, and k' is the proportionality constant relating S to t. To correct b, the following equation should be used:

$$b_{\text{corr.}} = P'' \times k \qquad \text{(Eq. 7)}$$

where P'' is the potentiometer setting represented by $+5\ V$ in Fig. 1, and k is the proportionality constant relating F to V. Thus for the systems investigated $b_{\text{corr.}} = 5\ V \times 100 = 500$. The corrected values for a, b, and c may now be substituted into Eq. 3 to give an equation which completely describes the pseudoplastic rheogram.

Since the Stormer viscosimeter was used in the present study, it should be pointed out that the constants obtained by computer fit of these data will be different from those obtained from data accumulated from another viscosimeter. However, the general equation and the computer program are applicable regardless of the instrument employed.

DISCUSSION

The empirical log-log plot frequently used to describe pseudoplastic flow very often does not truly characterize the experimental curve. It is not unusual for this type of plot to produce a great deal of scatter in the points or even another curved line.

[1] Manufactured by Electronics Associates, Inc.
[2] Manufactured by Hewlett-Packard, Inc.

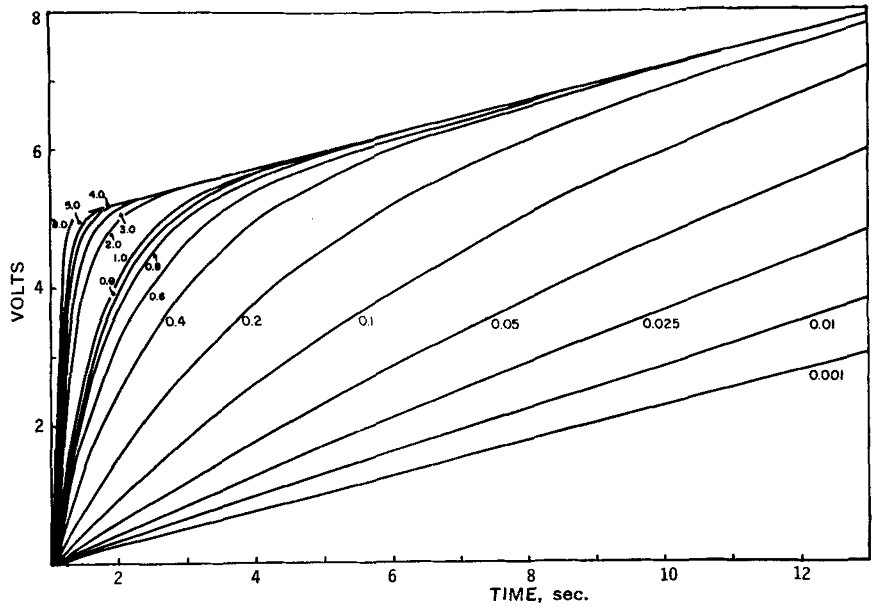

Fig. 2—Effect of variation of c *(*a *= 0.3) on the shape of pseudoplastic flow curves.*

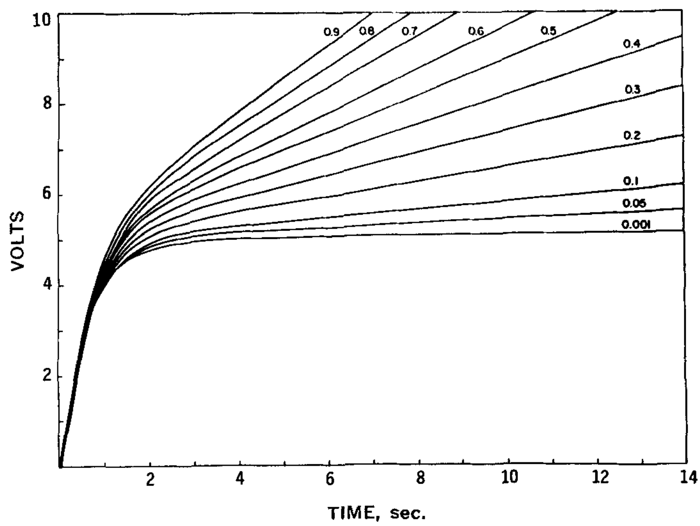

Fig. 3—Effect of variation of a *(*c *= 1.0) on the shape of pseudoplastic flow curves.*

TABLE I—RHEOLOGICAL DATA FOR VARIOUS CMC MUCILAGES

2.8% w/w		2.2% w/w		1.6% w/w	
Gm.	r.p.m.	Gm.	r.p.m.	Gm.	r.p.m.
250	45.5	100	38.9	40	40.9
300	58.6	120	49.1	50	53.2
350	72.3	150	65.0	60	66.0
400	91.4	175	80.8	80	92.2
500	127	200	94.4	100	120
650	198	250	128	150	195
800	286	300	163	200	286
900	351	400	238	250	373
		500	328		

The slope of this "line" yields a so-called index of pseudoplasticity.

The method proposed in this study offers three parameters to describe the experimental data and characterize the entire flow curve quantitatively. While the approach is still admittedly empirical, no difficulty has been encountered in successfully characterizing any of the experimental data employed. Figure 4 clearly demonstrates that a wide variety of pseudoplastic curves can be accurately simulated.

It is realized that not all rheologists can count an analog computer as one of the research tools commonly at his disposal in the laboratory. Nevertheless, almost every research investigator in rheology, whether in industrial or academic circles, has an analog computer within reasonably easy reach. The computer program presented here is a model of simplicity, mastery of which would require no

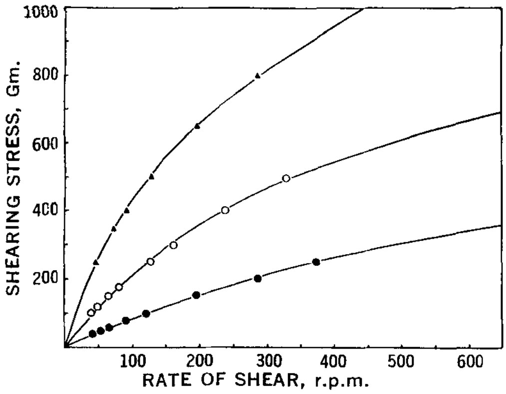

Fig. 4—Computer fits of actual data for CMC flow curves. Computer scale: 1 v. = 100 Gm. and 1 sec. = 50 r.p.m Lines represent computer fit and points represent the actual rheological data. Key: ▲, *2.8%;* ○, *2.2%;* ●, *1.6%.*

TABLE II—VALUES OF a AND c OBTAINED FROM COMPUTER DATA TO FIT VARIOUS CMC RHEOGRAMS

% w/w CMC	a	c	$a_{corr.}$	$c_{corr.}$
2.8	0.55	0.55	1.10	1.10×10^{-2}
2.2	0.165	0.225	0.33	4.5×10^{-3}
1.6	0.01	0.09	0.02	1.8×10^{-3}

more than 30 min. instruction even to those completely alien to computer programming.

In summary, this paper has presented a method for the quantitative determination of three parameters which completely characterize the shape of pseudoplastic flow curves. Evidence has been presented regarding the general applicability of the method by making use of actual experimental data. The method is rapid and avoids any extensive calculations. It is hoped that the use of this procedure will lead to a common means of communication among rheologists, working with pseudoplastic systems, who wish to compare experimental data. It is also possible that with the aid of the analog computer some new light may be thrown on the mechanism of pseudoplastic flow. There is a distinct possibility that the same type of treatment presented here may be applied to other rheological systems. Work in these areas is being pursued at the present time.

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Keyphrases

Rheology
Pseudoplastic flow simulated by analog computer
CMC mucilage systems
Analog computer diagram
Simulated system-CMC mucilage comparison flow curves

Apparent pH Dependence of Ethanol Absorption Rate in the Common Guppy

By WILLIAM L. HAYTON and NATHAN A. HALL

The uptake of ethanol from buffered solution by guppies has been studied. There was an apparent increase in the rate of absorption with increasing pH. In contrast, similar experiments made with goldfish failed to show an increase in absorption rate as the pH was increased. The guppy should be used with caution as a model for investigating the effects of varying pH upon drug absorption.

FISH ARE widely used for experimental purposes and for biological assays and have been used for a variety of biological studies including outstanding works in experimental embryology, endocrinology, and nerve physiology (1). The gross anatomy and physiology of fish are comparable to that of mammals, and fish contract many of the same diseases as do mammals. Fish have become popular as experimental tools because they are relatively inexpensive and easily kept in the laboratory.

The use of fish in drug absorption studies has led to the development of a theory by Levy and Gucinski (2) describing the uptake of drugs from a bathing solution by goldfish. The theory describes the uptake of drugs by fish under appropriate conditions as a simple diffusion process dependent upon the concentration of the drug in the external bathing solution.

Received July 6, 1967, from the College of Pharmacy, University of Washington, Seattle, WA 98105
Accepted for publication September 11, 1967.
This article is based in major part upon a manuscript for which William L. Hayton was the recipient of the Lunsford Richardson Pharmacy Award for Region I, 1967.