Stabilizing Effects of Surfactants on Pseudoplastic Falling Films

The effects of nonionic surfactants on thin-film flow of pseudoplastic non-Newtonian liquids down a smooth vertical plate have been studied experimentally. For all liquids examined there was a surfactant concentration at which the stabilizing action of surfactants was maximized. Comparison with experimental data showed that an existing equation, developed for the stabilizing action of surfactants on thin-film flow of Newtonian fluids, may be used to predict the effect of surfactants on the stability of pseudoplastic thin-film flow by using the zero-shear rate apparent viscosity in place of the Newtonian viscosity.

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SCOPE

The flow of viscous liquids in thin films down a vertical plate under the influence of gravity and surface tension is of both fundamental and practical importance in a wide variety of separation and heat transfer processes. The occurrence of waves on the film surface is known to enhance greatly the rates of mass, heat, and momentum transfer. The film flow pattern, however, is often modified by the presence of impurities that can act as surface active agents at the film free surface. A macroscopic action of surfactants on the film flow is the damping of waves, which reduces the rates of transport processes (Levich, 1962, for example). A significant number of studies has been reported on the influence of surfactants on the flow of Newtonian thin films and these are reviewed in Tailby and Portalski (1961) and Strobel and Whitaker (1968). A rather complex mathematical analysis has led Whitaker (1964) to the Equation (1), cited below, which provides a criterion for Newtonian film stability, in the limiting case of insoluble surfactants. No such work has appeared on non-Newtonian film flow although differences occur in both the constitutive equation and the liquid behavior at the film free surface. This work was performed to provide the first experimental data needed for an understanding of the effect of surfactants on pseudoplastic film flow down a vertical plate and to consider whether Equation (1) can be applied to predict the stabilizing effect of surfactants on pseudoplastic falling films. Pseudoplastic liquids were selected because they are encountered more in practice than other types of non-Newtonian liquids.

CONCLUSIONS AND SIGNIFICANCE

It was found in this work, by comparing experimental data with Equation (1), that this equation can be applied to predict the stabilizing effect of surfactants on pseudoplastic film flow by using the apparent viscosity at zero-shear rate in place of the Newtonian viscosity. There is no reason to believe that this conclusion is not applicable to all inelastic non-Newtonian liquids without yield stress. This is of practical importance because it avoids mathematical complexities that would arise in an analytical treatment similar to the one which led to Equation (1), using constitutive equations for non-Newtonian liquids.

For the liquids and surfactants studied, there exists a surfactant concentration for which the stabilizing effect is maximized, similar to the findings on Newtonian falling films (Tailby and Portalski, 1961).

Surfactants, when present in the liquid, are constantly redistributed between the bulk of the liquid and the surface due to both the surface wave motion and the adsorption-desorption kinetics at the surface. The consequent variation in concentration along the film surface causes surface tension gradients which stabilize the film by opposing the deformation of the interface (Levich, 1962). There is, however, no agreement upon whether surfactants stabilize flow so that waves are not present below a certain flow rate for a given liquid and given surfactant, or whether the growth rate of waves is reduced to the point where they are merely invisible in the usual type of experiment (Strobel and Whitaker, 1968). In a theoretical study on the effect of surfactants on Newtonian film stability, for the limiting case of insoluble surfactants, Whitaker (1968) showed that a critical Reynolds number, "that is a Reynolds number below which the flow is stable to all disturbances" is given by

$$Re_i = 1.68 \left[\frac{\left(\frac{\partial \sigma}{\partial \Gamma} \right)^3}{\rho^3 \nu^4} \right]^{1/5} \tag{1}$$

where $\partial\sigma/\partial\Gamma$ is termed *surface elasticity* and is related to the tangential stress at the film surface (Levich, 1962):

$$(\tau_{12})_{\text{surf.}} = -\frac{\partial \sigma}{\partial \Gamma} \operatorname{grad} \Gamma \tag{2}$$

The surface tension σ is a function of surfactant surface concentration Γ which itself is a function of position at the film surface. The Reynolds number is defined as

$$Re = \frac{4Q}{\mu} \tag{3}$$

where Q is the liquid mass flow rate per unit width of the plate, μ is viscosity, and ν kinematic viscosity. The governing equations that had to be considered simultaneously (Whitaker, 1964) were transport of momentum and mass for the bulk and the surface fluids. Although consideration was confined to a Newtonian liquid, the author found the problem to be highly complex. The use of a constitutive equation of non-Newtonian liquids can only increase the difficulties in a mathematical treatment of the problem. At this point we have examined the extent to which the results obtained from a theoretical analysis on Newtonian thin-film flow can be applied to film of inelastic non-Newtonian liquids. In particular we consider whether Equation (1) can be used to predict the stabilizing effect of surfactants on thin film flow of pseudoplastics and what shear property of these liquids must be used. The effect of surfactants is primarily a surface action, and it is natural to expect that the liquid shear property, viscosity, should be considered at the film surface shear conditions, which means at the conditions of virtually zero shear rate. To find out whether this expectation is right, one has to consider other possible choices of viscosity functions, commonly used in work on non-Newtonian liquids, and to compare with experimental data.

The constitutive equation of the pseudoplastic liquids in viscometric flow is given by

$$\tau_{12} = K(\dot{\gamma})^n \tag{4}$$

where τ_{12} is the shear stress, K is the consistency factor, γ is the rate of shear, and $0 < n < 1$ is the flow behavior index.

EXPERIMENTAL RESULTS

The apparatus used resembles that described in (Tailby and Portalski, 1961). As a vertical plate a glass mirror 50 cm wide and 180 cm long was used. Standard care of constant level head, knife-edge top of the plate, and of isothermal conditions has been taken. The surface area of the plate was large enough to provide accurate measurements of the average film velocity and thickness by measuring the liquid hold-up on the plate. The confidence in the hold-up measurements has been checked by running 30 runs with water for 3 different flow rates. The mean percent deviation was 0.82%. The use of the glass mirror as a plate enables sensitive observations of the film characteristics.

Neutralized aqueous solutions of CARBOPOL 934 (B. F. Goodrich) were used as pseudoplastic liquids. They provided constant flow behavior index n for a given liquid in the range of shear rates studied. Both K and n could be changed at will by changing the polymer concentration. An advantage that these solutions offered was that surface tension was not a function of polymer concentration and remained at the value for water. The rheological constants K and n of carbopol solutions were measured by Brookfield viscometer with a straight spindle.

Surfactants used in this work were nonionic Triton X-100 and Triton CF-10 (Rohm and Haas), condensates of ethylene oxide with an octylphenol. Their physiochemical properties are described in suppliers booklets. The surface tension of solutions was measured by a Kruss du Nouy Tensiometer. Exactly prepared concentratons of surfactants were checked on the spectrophotometer.

The stabilizing effects of surfactants on the film flow as a function of surfactant concentration has been determined by measuring the flow rate and film thickness (that is, Reynolds number) corresponding to the first visible waves at the film surface for every concentration of surfactant, the method used in Tailby and Portalski (1961). Experimental results are shown in Figures 1, 2, 3, and 4. It is seen that there exists, in all cases, a surfactant concentration for which the stabilizing action is a maximum. Maximum at the curve for critical Reynolds number falls at the beginning of the flat part of the curve surface tension versus surfactant concentration. This could be observed from data reported by Tailby and Portalski (1961) on Newtonian thin film flow, but not from data of Davies and Vose (1965) on damping of waves on a deep liquid. It was calculated by Ternovskaya and Belopolski (Fulford, 1964) that the surfactant concentration which maximizes wave damping corresponded to quantities of surfactant just sufficient to form a saturated monolayer at the interface. Maximum wave damping could be related to the observed minimum in mass transfer rates from droplets falling in another continuous liquid phase as a function of surfactant concentration (Skelland and Caenepeel, 1972).

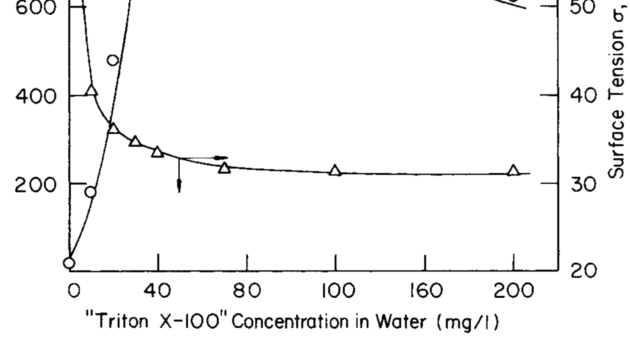

Fig. 1. Reynolds number of the first visible waves as a function of surfactant Triton X-100 concentration in water. ($T = 24.2°C$).

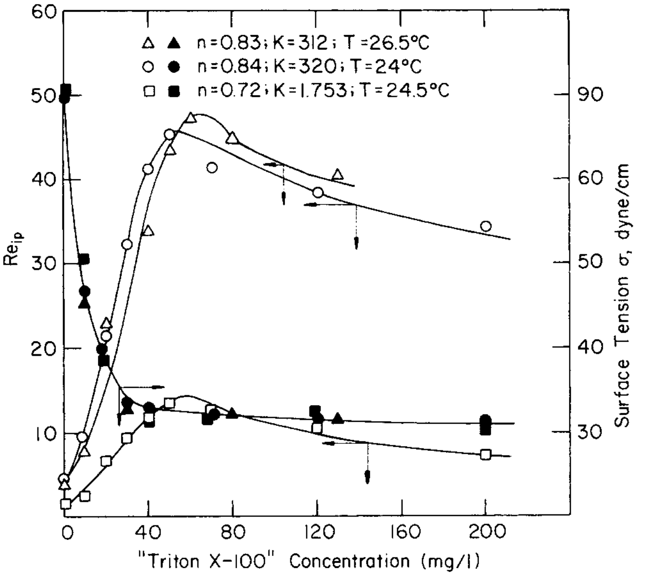

Fig. 2. Reynolds number of the first visible waves as a function of surfactant Triton X-100 concentration in aqueous carbopol solutions. (Solid points are surface tension data).

APPLICABILITY OF EQUATION (1)

It is evident from Figures 1 to 4 that the change of surface tension with surfactant concentration is virtually the same for water and for the pseudoplastic liquids studied, with minor differences due to small temperature variations during the experiments. Also, the shape of the curves for Reynolds numbers corresponding to the first visible disturbance on the film surface is practically the same for water and pseudoplastic liquids studied. The ratio of Re_i for a given pseudoplastic liquid to that of water calculated from experimental data is practically independent of surfactant concentration as shown in Figures 5 to 8. These facts allow us to assume that surface elasticity $\partial\sigma/\partial\Gamma$ for a given concentration of a particular surfactant could be considered to be the same for water and the pseudoplastic liquids studied. Measurements of surface elasticities is a fundamental question and the reader may see (Strobel and Whitaker, 1968) concerning that difficult task. To test Equation (1) for applicability to the film-flow of pseudoplastic liquids, the ratio of Re_i for water and pseudoplastic liquids could be used to eliminate the surface elasticity term:

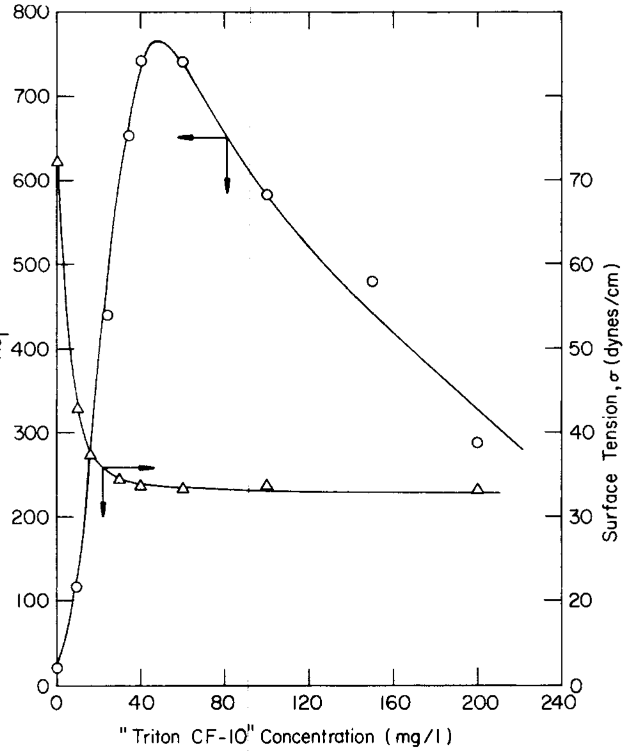

Fig. 3. Reynolds number of the first visible waves as a function of surfactant Triton CF-10 concentration in water. ($T = 28°C$).

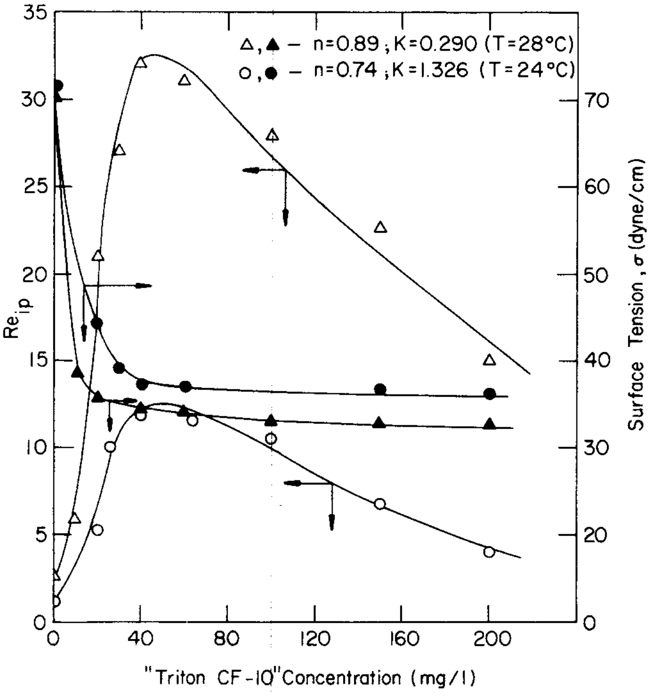

Fig. 4. Reynolds number of the first visible waves as a function of surfactant Triton CF-10 concentration in aqueous carbopol solutions. (Solid points are surface tension data).

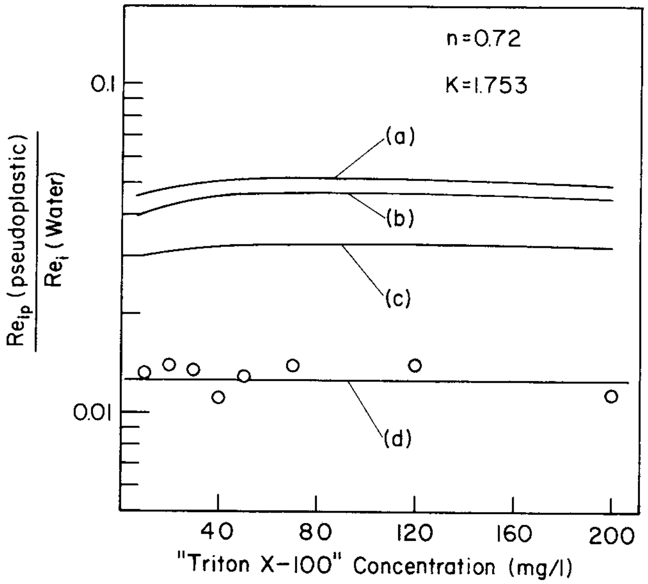

Fig. 5. Comparison of Equation (5) with the experimental data: (a) $\nu_p = \nu_a{}^0$, Equation (9); (b) $\nu_p = \nu_{ef.}$, Equation (11); (c) $\nu_p = \overline{\nu_a}$, Equation (10); (d) ν_p at zero-shear rate $\left(2.05 \frac{\text{cm}^2}{\text{s}}\right)$.

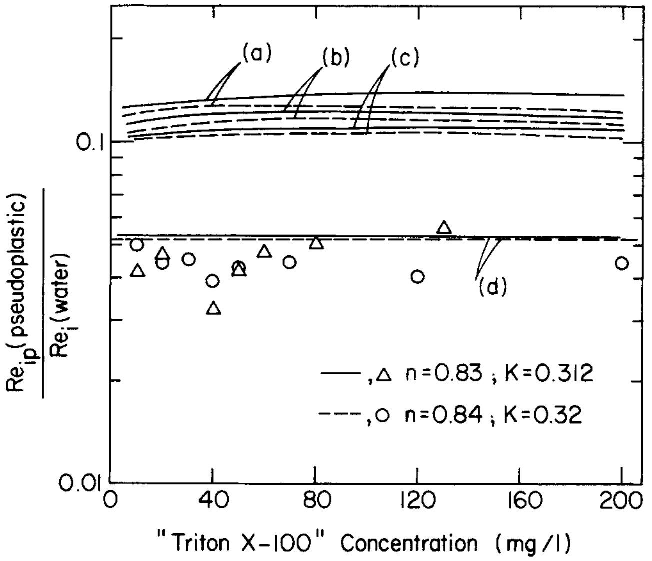

Fig. 6. Comparison of Equation (5) with the experimental data: (a) $\nu_p = \nu_a{}^0$, Equation (9); (b) $\nu_p = \nu_{ef.}$, Equation (11); (c) $\nu_p = \overline{\nu_a}$, Equation (10); and (d) ν_p at zero-shear rate $\left(0.362 \frac{\text{cm}^2}{\text{s}}\right)$.

$$\frac{Re_i\ (\text{pseudoplastic})}{Re_i\ (\text{water})} = \left(\frac{\rho_w{}^3 \nu_w{}^4}{\rho_p{}^3 \nu_p{}^4} \right)^{1/5} \tag{5}$$

Here the Reynolds number for pseudoplastics is defined by (Skelland, 1967)

$$Re_p = \frac{12n}{2n+1} \frac{Q}{g\delta} \left(\frac{\rho g \delta}{K} \right)^{1/n} \tag{6}$$

The kinematic apparent viscosity ν_p is a function of the shear rate, and hence of position across the film. In laminar film flow the shear stress at the film-quiescent gas interface is usually considered to be zero and the no slip condition at the plate leads to the following velocity profile:

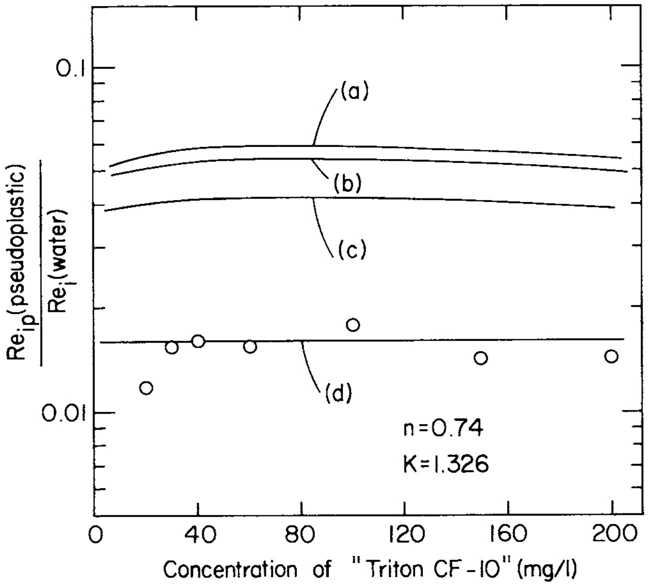

Fig. 7. Comparison of Equation (5) with the experimental data: (a) $\nu_p = \nu_a{}^0$, Equation (9); (b) $\nu_p = \nu_{ef}$., Equation (11); (c) $\nu_p = \bar{\nu}_a$, Equation (10); and (d) ν_p at zero-shear rate $\left(1.580 \frac{\text{cm}^2}{\text{s}}\right)$.

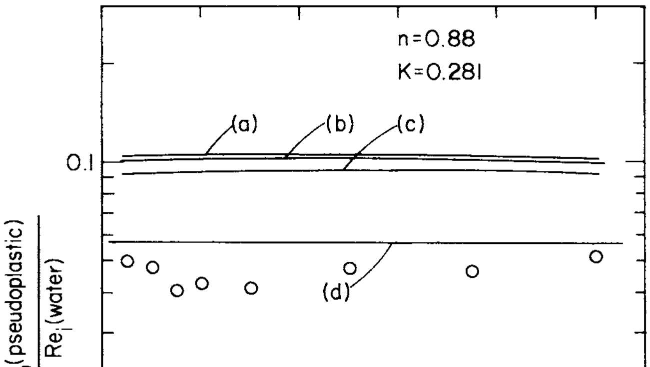

Fig. 8. Comparison of Equation (5) with the experimental data: (a) $\nu_p = \nu_a{}^0$, Equation (9); (b) $\nu_p = \nu_{ef}$., Equation (11); (c) $\nu_p = \bar{\nu}_a$, Equation (10); and (d) ν_p at zero-shear rate $\left(0.320 \frac{\text{cm}^2}{\text{s}}\right)$.

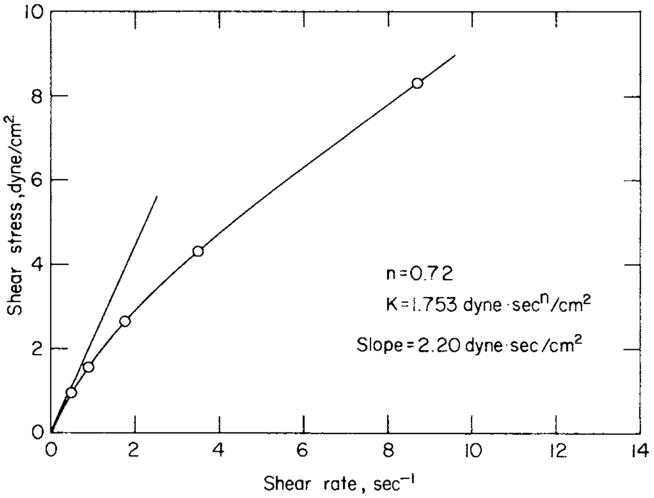

Fig. 9. A typical shear stress-shear rate curve for fluids studied.

$$u = \left(\frac{\rho g}{K} \right)^{\frac{1}{n}} \frac{n}{n+1} \delta^{\frac{n+1}{n}} \left[1 - \left(\frac{y}{\delta} \right)^{\frac{n+1}{n}} \right] \tag{7}$$

where δ is the film thickness and y is the coordinate normal to the film surface with the origin at the film surface. From (4) and (7) the apparent kinematic viscosity is then given by

$$\nu_a = \left(\frac{K}{\rho} \right)^{\frac{1}{n}} (gy)^{\frac{n-1}{n}} \tag{8}$$

Equation (8) gives local values and two other forms of it may be considered: the value of ν_a at the plate surface

$$\nu_a{}^0 = \frac{K^{\frac{1}{n}}}{\rho} (g\delta)^{\frac{n-1}{n}} \tag{9}$$

and the value of ν_a averaged across the film thickness,

$$\nu_a = \frac{1}{\delta} \int_0^\delta (\nu_a)\, dy \tag{10}$$

the effective viscosity could also be used (Skelland, 1967). This is the viscosity which in tube flow makes Poiseuille's equation fit laminar flow conditions. Applied to film flow it gives

$$\nu_{ef} = \frac{2n+1}{3n} \left(\frac{K}{\rho} \right)^{\frac{1}{n}} (g\delta)^{\frac{n-1}{n}} \tag{11}$$

These three possibilities, as well as the viscosity at the film surface condition of zero shear rate, are used here to compare Equation (5) with the experimental data. Zero-shear rate viscosity is determined as the slope on the shear stress-shear rate experimental curve at $\gamma = 0\ \text{s}^{-1}$, as is shown for one of the liquids in Figure 9.

Comparison of Equation (5) with the experimental data using these four possibilities for the pseudoplastic kinematic viscosity ν_p is presented in Figures 5 to 8. It is evident from the figures that the use of the kinematic apparent viscosity at the plate, Equation (9), gives the biggest deviation from the experimental data. This is because it represents the shear conditions furthest from the film surface. Also, use of the average kinematic apparent viscosity [Equation (10)] and the effective viscosity [Equation (11)], which both can represent the bulk fluid conditions, is inadequate in all cases. The best agreement with the data is provided by the use of zero-shear rate viscosity. The agreement is very satisfactory and provides considerable support for the use of Equation (1) to estimate stabilizing action of surfactants on pseudoplastic falling films.

NOTATION

g = gravitational acceleration, cm/s^2
K = consistency factor, (dyne s^n)/cm^2
n = flow index, dimensionless
Q = liquid mass flow rate per unit width of plate, g/cm s
u = liquid local velocity in the film, cm/s

Greek Letters

Γ = surfactant surface concentration, mole/cm^2
$\dot{\gamma}$ = rate of shear, s^{-1}
δ = film thickness, cm
μ = viscosity, g/cm s
ν = kinematic viscosity, cm^2/s
ρ = liquid density, g/cm^3
σ = surface tension, dyne/cm
τ_{12} = shear stress, dyne/cm^2

Subscripts

p = pseudoplastic
w = water
a = apparent
ef = effective

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Quadratically Convergent Techniques in Linearly Constrained Optimization

Methods for the solution of linearly constrained optimization of a nonlinear objective function are presented and compared. The methods of Fletcher-Reeves, Fletcher, and Powell are used to generate search directions in the decision variable space. Generalized Kuhn-Tucker conditions are presented and used to check for a local minimum.

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SCOPE

The objective of this work was to develop an approach to the minimization of nonlinear objective functions subject to linear equality and inequality constraints such that any effective unconstrained minimization technique could be employed to determine the search directions. Such a general approach would allow the immediate application of new unconstrained methods to linearly constrained problems. A number of significant chemical engineering problems fit this mathematical pattern, for example, determination of chemical equilibrium with competing reactions by minimization of the free energy subject to conservation of mass constraints.

Previous approaches (Goldfarb and Lapidus, 1968; Wolfe, 1963, 1967a, 1967b) to this problem were specific to certain search techniques and did not make use of generalized Kuhn-Tucker conditions which remove the requirement that independent variables be bounded to the positive region. Abadie (1970) considered the generalized Kuhn-Tucker conditions in his treatment of the general nonlinear programming problem but did not take advantage of the special treatment which can be given linear constraints.

CONCLUSIONS AND SIGNIFICANCE

The objective was accomplished as illustrated by the successful application of the unconstrained methods of Fletcher-Reeves (1964), Fletcher (1970), and Powell (1964) to a series of linearly constrained problems. Application of Powell's method is particularly significant since the user is not required to provide expressions for the derivatives of the objective function as in the other methods. Additionally, the results presented here may be used to improve generalized nonlinear programming techniques which are based upon repetitive linear programming in that the nonlinear nature of the objective