Burnett, R., DDT Residues: Distribution of Concentrations in Emerita Analogs Along Coastal California," Science, 174,

Draper, N. R., and H. Smith, Applied Regression Analysis,

Wiley, New York (1966). Gustafsom, C. G., "PCB'S—Prevalent and Persistent," Environ. Sci. Tech., 4, 814 (1970).

Hsiang, T., and P. M. Reilly, "A Practical Method for Descriminating Among Mechanistic Models," Can. J. Chem. Eng., **49**, 865 (1971).

Jacques, J. A., Compartmental Model Building in Biology and Medicine, Elsevier, New York (1973).

Keinath, T. M., (Ed.), "Mathematical Modeling in Environmental Engineering," Assoc. of Environmental Eng. Profs. Workshop, Nassau, Bahamas (1972).

Kenaga, E. E., "Guidelines for Environmental Study of Pesticides: Determination of Bioconcentration Potential," Residue

Rev., 44 73 (1972). Kittrell, J. R., "Mathematical Modeling of Chemical Reactions," Adv. Chem. Eng., 8, 99 (1970).

Neely, W. B., D. M. Branson, and G. E. Blau, "Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish," Environ. Sci. Tech., 8, 1113 (1974).

Patten, B. C., (ed.), Systems Analysis and Simulation in

Ecology, Academic Press, New York (1971). Quarles, J., "Criteria for Selecting Toxic Pollutants in Water," Fed. Register, 38, 24342 (1973)

Reilly, P. M., and G. E. Blau, "The Use of Statistical Methods to Build Mathematical Models of Chemical Reacting Sys-

tems," Can J. Chem. Eng., 52, 289 (1974).
Schaeffer, C. H., and E. F. Dupras, Jr., "Factors Affecting the Stability of Dursban" in Polluted Waters," J. Econ. Entomol., 63, 701 (1970).

Smith, G. N., B. S. Watson, and F. S. Fisher, "The Metabolism of [C14]0,0-Diethyl-0-(3,4,6-trichloro-2-pyridyl) phosphorthorate(Dursban) in Fish," ibid., 59, 1464 (1966)

Smith, G. N., "Basic Studies on Dursban" Insecticide," Down to Earth, 22, 3 (1966).

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Pseudoplastic Falling Films with Concurrent Gas Streams

An experimental and theoretical study on gas and pseudoplastic liquid films in vertical downward flow is reported. Good agreement was obtained between predicted and measured values of the film thickness as a function of liquid shear properties and interfacial shear except in the case of the most dilute solution. Measured pressure drops in the gas in two-phase flow depend strongly on liquid shear properties and are up to five times higher than when gas flows alone.

Aqueous Carbopol solutions were used as pseudoplastic liquids.

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SCOPE

The industrial significance of gas-liquid film flow has inspired many experimental and theoretical studies. Most published work deals with Newtonian films, and no such investigation has appeared on non-Newtonian liquids as far as we know. Non-Newtonian liquids, however, are increasingly involved in food engineering, polymer processing, suspension and emulsion processing, and bioengineering. This work has been conducted to provide experimental evidence on the behavior of a pseudoplastic thin film flowing in parallel with an adjacent gas stream. When

high shear is imposed at the gas-liquid interface, the film velocity profile depends strongly not only on liquid flow rate and shear properties but also on the interfacial shear. This makes an analytical solution of the momentum equations highly complex when dealing with non-Newtonian liquids. A semi-empirical method developed by Dukler (1959) for gas-Newtonian film flow is here extended to a gas-pseudoplastic film flow. Pseudoplastic liquids were selected because they are encountered more in practice than most other types of non-Newtonian liquids.

CONCLUSIONS AND SIGNIFICANCE

The experimentally determined dependence of film thickness on liquid shear properties, liquid flow rate, and gas velocity agrees satisfactorily with the theoretical predictions. Only in the case of the lowest concentration of Carbopol in water are the predicted values significantly higher. It is thought that a drag reduction effect might have been present and that it disappeared for higher con-

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centrations, as is known to occur for turbulent flow in

The wavy gas-liquid interface greatly enhances momentum transfer, and measured values of the gas-phase pressure drop were several times higher than when gas

It is of practical importance that a semi-empirical analysis successfully predicted the film thickness and its dependence on interfacial shear in gas-liquid flow.

EXPERIMENT

The apparatus resembles that described by Tailby and Portalski (1962) and Tyler (1971). As a vertical plate a glass mirror 34 cm wide and 180 cm long was used. Standard care of constant level head, knife-edge top of the plate, and of isothermal conditions was 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 holdup on the plate. The confidence in the holdup measurements has been checked by running 30 runs with water for 3 different flow rates. The mean deviation was 0.82%. The validity of this holdup procedure was also shown by Tyler (1971) for viscous aqueous glycerol solutions. The use of the glass mirror as a plate and a plexiglass cover sheet for the gas flow channel enabled sensitive observations of the film characteristics. There were no local measurements of gas velocities. The gas flow rate was measured with a standard orifice meter and the average gas velocity calculated from the cross section based on $H^1 - \delta_0$, where H^1 is the distance between the mirror and the plexiglass plate (1.587 cm). The local problems of the moving gas-liquid interface are beyond the scope of this work (Dukler, 1972).

As pseudoplastic liquids, aqueous solutions of Carbopol 934 (B. F. Goodrich Chemical Company) were used. This choice was made because aqueous Carbopol solutions offered several advantages. They obey the power-law constitutive equation over the range of shear rates and concentrations studied. The consistency index and flow behavior index could be changed at will by changing the polymer concentration and the pH of the solution. The surface tension of these solutions is independent of polymer concentration and remains virtually at the value for water. The molecule has only short side branchings and is not greatly susceptible to shear degradation. Aqueous Carbopol solutions were reported to be free from elastic effects for low polymer concentrations (Bogue and Metzner, 1963). The constitutive equation for these liquids in a viscometric flow has a simple form

$$\tau = K \left(\dot{\gamma} \right)^n \tag{1}$$

where K and n are consistency factor and flow behavior index, respectively, and $\dot{\gamma}$ is the rate of shear. The rheological constants K and n were measured with a Brookfield viscometer with a straight spindle.

Air was used as the gas stream. The air velocities applied were up to 15 m/s. Each of our data points is an average of 3 to 4 measurements.

ANALYSIS

A macroscopic momentum balance on the film gives

$$\tau_0 = \rho_L g \delta_0 + \left(\rho_G g - \frac{dP}{dL}\right) \frac{H}{2} \tag{2}$$

$$\tau = \rho_L g \left(\delta_0 - y \right) + \left(\rho_G g - \frac{dP}{dL} \right) \frac{H}{2} \tag{3}$$

where τ_0 and τ are wall shear stress and shear stress at any position in the film, respectively, (dP/dL) is the gas pressure gradient, and $H = H^1 - \delta_0$, with H^1 being the distance between the two vertical planes which form the channel for gas-liquid film flow, δ_0 is the film thickness, and y is the coordinate normal to the film flow. Note that practically $H^1 = H$ for a thin film.

Together with the momentum balance, a macroscopic mass balance has to be considered:

$$Q = \int_0^{\delta_0} u \ dy, \tag{4}$$

In terms of universal parameters, that is,

$$u_* = \left(\frac{\tau_0}{\rho_L}\right)^{\frac{1}{2}}$$
; $u^+ = \frac{u}{u_*}$; $y^+ = \frac{y^n u_*^{2-n} \rho_L}{K}$ (5)

Equation (2) gives

$$\left(\frac{K\delta_0^+}{\delta_0^n \rho_L}\right)^{\frac{2}{z-n}} = \delta_0 g + \left(\frac{\rho_G g - dP/dL}{\rho_L g}\right) \frac{gH}{2} \quad (6)$$

After a few rearrangements, Equation (6) can be written in a convenient form

$$\sigma^{\frac{n+2}{2-n}} + \left[\beta/(\delta_0^+)^{\frac{2n}{2-n}}\right] \sigma^{\frac{2n}{2-n}} - 1 = 0 \tag{7}$$

where the dimensionless interfacial shear β is

$$\beta = H \left[\frac{\rho_G g - dP/dL}{\rho_L g} \right] g^{\frac{2-n}{n+2}} \rho_L^{\frac{2}{n+2}} / 2 K^{\frac{2}{n+2}}$$
 (8)

and

$$\sigma = \delta_0 g^{\frac{2-n}{n+2}} / \left(\frac{K \delta_0^+}{\rho_L}\right)^{\frac{2}{n+2}}$$
(9)

The dimensionless interfacial shear β takes into account the gas-phase pressure drop, liquid properties, and channel geometry. From Equations (2) and (3), an equation for shear stress distribution in terms of σ and δ_0^+ can be written in the following convenient form:

$$\frac{\tau}{\tau_0} = 1 - \left(\frac{\frac{n+2}{\sigma^{2-n}}}{(\delta_0^+)^{1/n}}\right) (y^+)^{1/n} \tag{10}$$

As usual, to make practical use of the equation for shear stress distribution, a relationship between stress and velocity gradient is needed. As done by Dukler (1959), we do not anticipate a priori either laminar or turbulent flow. For pseudoplastic liquids, then, we have

$$\tau = K \left(\frac{du}{dy}\right)^n + \rho_L \epsilon \frac{du}{dy} \tag{11}$$

It is necessary now to have an expression for the eddy viscosity. In his original work on Newtonian falling films, Dukler (1959) used Deissler's expression for $y^+ \leq 20$, developed for the eddy viscosity of flow in full tubes. As suggested by Dukler and justified in this work, the dimensionless film thickness does not exceed 20, and for pseudoplastic liquids we suggest that Deissler's expression is applicable to $y^+ \leq 20^n$ and that the expression takes the form

$$\epsilon = m^2 u y \left\{ 1 - \exp \left[-\frac{m^2 u y}{\tau_0^{\frac{n-1}{n}} (K/\rho_L)^{1/n}} \right] \right\}$$
(12)

where m is a numerical constant determined by Deissler from the tube flow velocity distribution; m = 0.124. The justification for this suggestion is left until the comparison with experimental data.

In terms of universal parameters, after substitution of Equations (11) and (12) into (10), an equation for the velocity distribution across the film is obtained

$$1 - \left[\frac{\sigma^{\frac{n+2}{2-n}}}{(\delta_0^+)^{1/n}}\right] (y^+)^{1/n} = (n)^n (y^+)^{n-1} \left(\frac{du^+}{dy^+}\right)^n + m^2 n u^+ y^+ \left[1 - \exp\left(-m^2 u^+ (y^+)^{1/n}\right)\right] \frac{du^+}{dy^+}$$
(13)

Deissler's equation was developed for use in the neighborhood of solid surfaces, and for film flow in the neigh-

borhood of the plate $u^+ \to 0$ and $y^+ \to 0$ so that also $[1 - \exp(-m^2 u^+ (y^+)^{1/n}] \to 0$ and the velocity distribution is given by

$$u^{+} = \int_{0}^{y^{+}} \left\{ (n)^{-n} (y^{+})^{1-n} - \left[\frac{\frac{n+2}{\sigma^{2-n}}}{(\delta_{0}^{+})^{1/n}} \right] (y^{+})^{\frac{1-n^{2}+n}{n}} (n)^{-n} \right\}^{1/n} dy^{+}$$
 (14)

We also express the mass balance, Equation (4), in terms of universal parameters:

$$Q = \frac{1}{n} u^{\frac{2n-2}{n}} \left(\frac{K}{\rho_L}\right)^{1/n} \int_0^{\delta_0^+} u^+ (y^+)^{\frac{1-n}{n}} dy^+$$
(15)

This expression is readily related to the liquid Reynolds number, which could be defined as (Skelland, 1967)

$$Re = \frac{12n}{2n+1} \left(\frac{Q}{g\delta_0}\right) \left(\frac{\rho_L g\delta_0}{K}\right)^{1/n}$$
 (16)

Also an expression for the film thickness is obtained from Equation (9)

$$N_{\delta} = \sigma \left(\delta_0^+\right)^{\frac{2}{n+2}} \tag{17}$$

where

$$N_{\delta} = \delta_0 \left[\left(\frac{\rho_L}{K} \right)^2 g^{2-n} \right]^{\frac{1}{n+2}}$$
 (18)

We have obtained equations which express the dependence of the film thickness on liquid flow rate and shear properties, as well as on the interfacial shear, but the calculation is quite lengthy. Equations (7), (14), (15), and (17) have to be solved simultaneously. For numerical integrations the Continuous System Modeling Program (CSMP), version 1.3, for the IBM/360 computer, was applied. Tabulated numerical and experimental data may be found elsewhere (Popadic, 1974). For n = 1 the analysis reduces to Dukler's analysis for Newtonian liquids. This case is compared with the experimental data for zero interfacial shear in Figure 1. Very good agreement is obtained, which is of particular significance for higher values of Re. The dependence of the film thickness on interfacial shear for water is shown as the dependence of δ_0 on the air velocity in Figure 2. For each

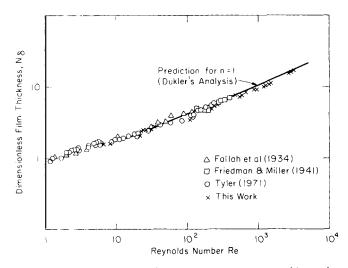


Fig. 1. Dependence of the film thickness on liquid Reynolds number for Newtonian liquids (no gas flow).

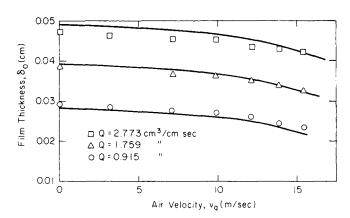


Fig. 2. Dependence of the film thickness on gas velocity (liquid: water).

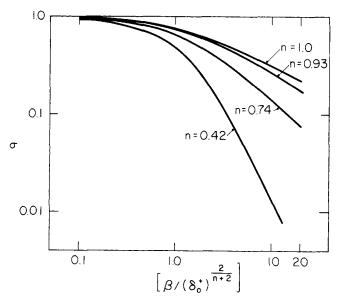


Fig. 3. The solution of Equation (7) for liquids studied.

air velocity and liquid flow rate the air pressure drop was measured, from which values of dimensionless interfacial shear were calculated and corresponding theoretical values of δ_0 determined as described. The predicted dependence of σ , and hence δ_0 , on the interfacial shear for the pseudoplastic liquids studied is shown in Figure 3. It is seen that for a given value of the interfacial shear films become thinner when pseudoplasticity increases and that for a particular liquid the film thickness decreases when interfacial shear increases. Comparison with experimental data is shown in Figures 4, 5, and 6. The mean deviations are as follows:

	Liquid		Mean deviation, %
	Water		4.05
n = 0.930;	K = 0.124;	$C = 0.05\% \mathrm{w}$	(+)18.84
n = 0.740;	K = 1.444;	C = 0.10% w	4.82
n = 0.417;	K = 7.048;	C = 0.16%w	4.28

 $^{\rm o}$ The relative deviation is defined as Rd = (predicted-experimental)/ experimental.

It is seen that the biggest deviation is in the case of the lowest concentration of Carbopol in water. It seems that in this case an effect of drag reduction may be occurring so that the liquid flows faster than expected for the given gas flow rate. For higher concentrations this postulated drag reduction effect disappears, as is known to occur for

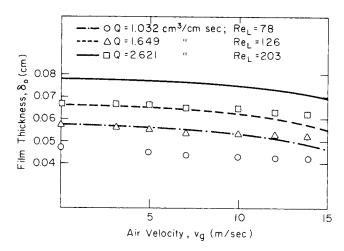


Fig. 4. Dependence of the film thickness on air velocity. Liquid: $n=0.930;\,K=0.124.$

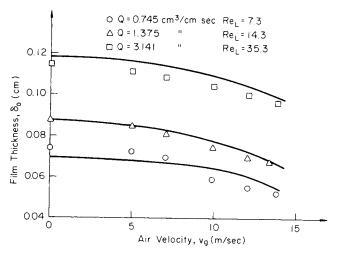


Fig. 5. Dependence of the film thickness on gas velocity. Liquid: $n=0.740;\,K=1.444.$

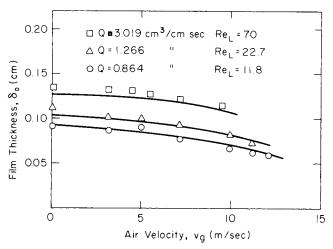


Fig. 6. Dependence of the film thickness on air velocity. Liquid: $n=0.417;\,K=7.048.$

turbulent flow in a tube, and the predicted film thickness agrees very well with experiment.

The agreement between predicted and measured film thicknesses allows an indirect judgment of velocity profiles in the film. Velocity profiles depend not only on the liquid flow rate and shear properties, but also on interfacial shear. In Figure 7 it is shown how velocity profiles depend on pseudoplasticity for the same dimensionless

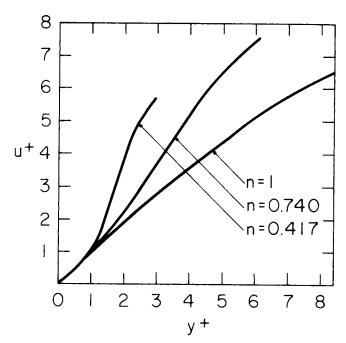


Fig. 7. Velocity profiles for liquids studied;

$$eta=1$$
 and $rac{rac{n+2}{\sigma^{2-n}}}{(\delta_0+)^{1/n}}=0.050$

interfacial shear and the parameter $\sigma^{\frac{n+2}{2-n}}/(\delta_0^+)^{1/n}$. The velocity is higher for the liquids with higher pseudoplasticity.

To calculate the interfacial shear for the prediction of film thicknesses, the air pressure drop was measured for every velocity of the air and a given liquid flow rate.

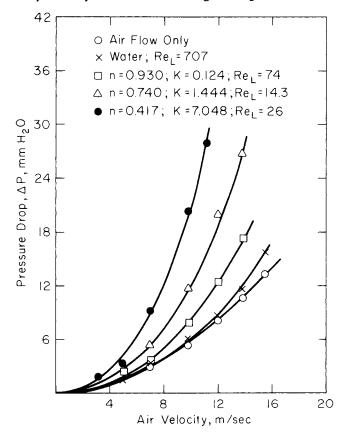


Fig. 8. Dependence of air pressure drop on liquid properties and gas velocity, ($\Delta L = 4$ ft.)

Some of the data are presented in Figure 8 to show that the gas phase pressure drop depends highly on liquid physical properties, much more than could be accounted for by the liquid Reynolds number. As is evident from the figure, pressure drop in the gas phase when a falling film is present is up to five times higher than when gas flows alone. Our observations during experiments were that a high level of gas velocity (> 10 m/s) is accompanied by the formation of somewhat regular rolling waves over the full width and length of the plate. Interfacial shear produces higher waves than those that already exist on the liquid film surface, and waves enhance the pressure drop. This effect was more pronounced for the case of liquids with higher apparent viscosities because larger film thicknesses allowed easier deformation of the surface. This problem of a moving gas-liquid interface is discussed in detail by Dukler (1972).

As far as we know, these are the first available data on gas-pseudoplastic film flow. It was thought, however, that the amount of data is not large enough to construct an empirical correlation for the dependence of gas-phase pressure drop on liquid shear properties.

NOTATION

 \boldsymbol{C} = Carbopol concentration in water, %w

= gravity acceleration, cm/s²

g H1 = distance between planes which form the channel for gas-liquid flow, cm

K = consistency factor, dyne sⁿ/cm²

 \boldsymbol{L} = length of plate, cm = flow behavior index

= liquid volume flow rate per unit width of the Q plate, cm3/cm s

= velocity of the liquid film, cm/s

= dimensionless liquid velocity, see Equation (5) u^+

= friction velocity, cm/s u. = gas velocity, m/s v_g

= coordinate normal to the film flow

= dimensionless distance from the wall, see Equation (5)

Greek Letters

= dimensionless interfacial shear

= rate of shear, s^{-1} = film thickness, cm

= value of y^+ at $y = \delta_0$ = density, g/cm³

= defined by Equation (9)

= shear stress, dyne/cm² = wall shear stress, dyne/cm²

Subscripts

= liquid phase

= gas phase

LITERATURE CITED

Bogue, D. C., and A. B. Metzner, "Velocity Profiles in Turbulent Pipe Flow," Ind. Eng. Chem. Fundamentals, 2, 143

Dukler, A. E., "Dynamics of Vertical Falling Film Systems," Chem. Eng. Progr., 55, 62 (1959).

, "The Wavy Gas-Liquid Interface," in Progress in Heat and Mass Transfer, Vol. 6, p. 207, Pergamon Press, New York (1972).

Fallah, R., T. G. Hunter, and A. W. Nash, J. Soc. Chem. Ind.,

53, 369T (1934); referred to in (Tyler, 1971).
Friedman, S. J., and C. D. Miller, "Liquid Films in the Viscous Flow Region," *Ind. Eng. Chem.*, 33, 885 (1941).
Popadić, V. O., "Pseudoplastic Thin-Film Flow," Ph.D. dis-

sertation, Univ. Kentucky, Lexington (1974).

Skelland, A. H. P., Non-Newtonian Flow and Heat Transfer, Wiley, New York (1967).

Tailby, S. R., and S. Portalski, "Wave Inception on a Liquid Film Flowing Down a Hydrodynamically Smooth Plate," Chem. Eng. Sci., 17, 283 (1962).

Tyler, J. S., "Non-Newtonian Thin Film Flow," Ph.D. disserta-

tion, Univ. Notre Dame, Indiana (1971).

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Grouping of Many Species Each Consumed by Two Parallel First-Order Reactions

The behavioral features of a mixture containing many species each of which participates in two competing parallel first-order reactions may deviate significantly from those of the individual species. For example, the grouped selectivity may depend on the conversion and attain up to N-2 extremal values where N is the number of the reactants in the mixture. The kinetics of the grouped species depends on the composition of the feed and can be of an unconventional functional form. The use of empirical grouped kinetics may lead to unexpected pitfalls. For example, grouped rate expressions based on experiments carried out in one reactor may not be adequate for predicting the behavior in a reactor with a different residence time distribution.

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