COMMUNICATIONS TO THE EDITOR

A Withdrawal Theory for Ellis Model Fluids

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Consider the prediction of wave-free, laminar entrainment in withdrawal of flat plates from pseudoplastic non-Newtonian liquids. These liquids have stress rate of shear properties which include a zero yield stress and an independence of time.

Many of these pseudoplastic fluids have rheological curves which can be represented well by three regions classified by stress (*4*). The low stress region is linear through the origin (Newtonian A), the intermediate stress region is linear on log-log coordinates (power law), and the high stress region is linear through the origin but different in slope (Newtonian B). In withdrawal of Carbopol solutions, it has been shown that stresses present were in both the low and intermediate regions but that the high stress region was not involved (*1*). Because of this experimental evidence, no constitutive equations involving high shear are considered here. Thus we consider fluids which can be approximated by the Ellis model constitutive equation over the region of low and intermediate stress.

The only previous attempt to predict theoretically the effect of surface tension in this withdrawal problem did not succeed. The magnitude of entrainment predicted by using a power law model was substantially larger than that observed in laboratory studies (*1*). Some progress was made, however, in the form of a semiempirical design equation which was based on theoretical functions and experimental coefficients. A deficiency of the power model is the neglect of the linear behavior of pseudoplastic fluids near zero stress, especially since low stress occurs near the surface of all withdrawal films. Therefore it seems reasonable to expect better agreement with a theory based on a constitutive model that includes rheological behavior near zero stress as well as at intermediate stress. One such model is the Ellis fluid.

A theoretical prediction for withdrawal from an Ellis fluid has been reported for the special case where surface tension effects are negligible. This negligible surface tension theory did not succeed when applied to power law data (*1*); it predicted magnitudes of entrainment which differed from data even more than the surface tension model. This negligible surface tension theory was derived by using the drainage approach. The two different methods of presentation (*1, 3*) have been found to be equivalent for Ellis fluids (*5*).

It is therefore the purpose of this note to present the first theory of withdrawal for Ellis fluids which includes the effect of surface tension. This is done by deriving the dynamic equation, making it dimensionless, solving the differential equation for dynamic curvature, and matching two predicted curvatures to obtain the theoretical solution.

DERIVATION OF THE DYNAMIC EQUATION (6)

We begin by writing the Ellis model as:

$$-\frac{du}{dy} = (a_0 + a_1{}^{\alpha} |\tau_{yx}|^{\alpha-1})\, \tau_{yx} \tag{1}$$

This form was chosen because it reduces directly to the power model (*5*).

Following the assumptions described elsewhere (*1*), we write the x component of the equation of motion and neglect inertial terms:

$$\rho g_x - \frac{\partial p}{\partial x} - \frac{\partial \tau_{yx}}{\partial y} = 0 \tag{2a}$$

Choosing the x axis as vertical upward and the y axis as perpendicular to and originating at the plate, we have $g_x = -g$. From Laplace, we have $p = -\sigma/R$ where R is the radius of curvature of a concave meniscus. We then take $\partial p/\partial x = -\sigma d^3h/dx^3$, which holds where $dh/dx < 1$ and where interfacial tension is constant. With these substitutions we obtain the starting equation:

$$-\rho g + \sigma \frac{d^3h}{dx^3} - \frac{\partial \tau_{yx}}{\partial y} = 0 \tag{2b}$$

We begin development of Equation (6) by simplifying Equation (2*b*) for integration at constant height x. Thus

$$\frac{\partial \tau_{yx}}{\partial y} + m = 0 \tag{2c}$$

where

$$m = \rho g + \frac{\partial p}{\partial x} = \rho g - \sigma \frac{d^3h}{dx^3} \tag{3}$$

With Equation (2*c*) and no shear at the interface we obtain the shear stress profile, $\tau_{yx} = m\,(h - y)$. Invoking the constitutive Equation (1) for the Ellis fluid and no slip at the wall, we obtain the velocity profile:

$$U = U_w - a_0\, m \left[hy - \frac{y^2}{2} \right] - \frac{(a_1\, m)^{\alpha}}{\alpha + 1} [h^{\alpha+1} - (h-y)^{\alpha+1}] \tag{4a}$$

From the definition of flux $Q = \int_0^h U dy$, the flux in the dynamic meniscus region 2 is

$$Q_2 = U_w h - \frac{a_0\, m h^3}{3} - \frac{(a_1\, m)^{\alpha}\, h^{\alpha+2}}{\alpha + 2} \tag{4b}$$

The flux in the constant thickness region 1 is obtained by using the condition of Equation (5a):

$$d^3h/dx^3 = 0 \quad \text{at} \quad h = h_o \tag{5a}$$

Thus

$$Q_1 = U_w h_o - \frac{a_0 \rho g h_o^3}{3} - \frac{(a_1 \rho g)^\alpha h_o^{\alpha+2}}{\alpha+2} \tag{5b}$$

By invoking continuity, one equates Q_1 and Q_2 or Equations (4b) and (5b) to obtain the desired third-order differential equation, which is

$$U_w h - \frac{a_0 m h^3}{3} - \frac{(a_1 m)^\alpha h^{\alpha+2}}{\alpha+2} = U_w h_o - \frac{a_0 \rho g h_o^3}{3} - \frac{(a_1 \rho g)^\alpha h_o^{\alpha+2}}{\alpha+2} \tag{6}$$

This is a new equation. It describes the dynamic meniscus in withdrawal from an Ellis fluid. The development of Equation (6) is a combined extension of the techniques used (*1*) for drainage without surface tension and for withdrawal without the low stress coefficient (a_0).

DIMENSIONLESS FORM OF THE DYNAMIC MENISCUS

Placing Equation (6) in dimensionless form required new approaches to select the additional parameters. After considerable trial and error, the following groups were selected:

Two dimensionless coordinates:

$$L = h/h_o \tag{7}$$

$$R_1 = -x/h_o \tag{8}$$

Two dimensionless thicknesses:

$$T_o = h_o \ (a_0 \rho g/U_w)^{1/2} \tag{9}$$

$$T_1 = h_o \left[(a_1 \rho g)^\alpha / U_w\right]^{1/(\alpha+1)} \tag{10}$$

And two dimensionless speeds:

$$C_o = U_w/a_0 \ \sigma \tag{11}$$

$$C_1 = (h_o^{\alpha-1} U_w/a_1 \ \sigma)^{1/\alpha} \tag{12}$$

The significance of these parameters is discussed below, together with substitution details. After grouping the m terms on the left-hand side, the dimensionless meniscus coordinate $L = h/h_o$ and dimensionless thicknesses T_o and T_1 were used. Here T_o is equivalent to that used for Newtonian fluids (*6*) and T_1 to that used for power law fluids (*1*). With these substitutions, Equation (6) becomes

$$\frac{a_0 m h^3}{3U_w h_o} + \frac{(a_1 m)^\alpha h^{\alpha+2}}{(\alpha+2) U_w h_o} = (L-1) + \frac{T_o^2}{3} + \frac{T_1^{\alpha+1}}{\alpha+2} \tag{13a}$$

By substituting the definition of m, expanding the left-hand terms, and using the definitions of R_1 and C_o, Equation (13a) becomes

$$\frac{L^3}{3C_o}\frac{d^3L}{dR_1^3} + \left(a_1 \rho g - a_1 \sigma \frac{d^3h}{dx^3}\right)^\alpha \frac{h_o^{\alpha+1} L^{\alpha+2}}{U_w(\alpha+2)} = (L-1) - \frac{T_o^2}{3}(L^3-1) + \frac{T_1^{\alpha+1}}{\alpha+2} \tag{13b}$$

Here R_1 is a dimensionless coordinate transformed to vertical *downward* by the negative sign so that R increases as L increases. The origin for vertical integration may be taken as $R_1 = 0$ at $L = 1$, or $x = 0$ at $h = h_o$. The C_o and C_1 terms are dimensionless speeds equivalent to those used for Newtonian (*6*) and power law fluids (*1*), respectively. Substituting C_1, T_1, R_1 and L into the a_1 terms in Equation (13b), one obtains the following desired dimensionless form of Equation (6):

$$\frac{L^3}{3C_o}\frac{d^3L}{dR_1^3} + \left[T_1^{\frac{\alpha+1}{\alpha}} + \frac{1}{C_1}\frac{d^3L}{dR_1^3}\right]^\alpha \frac{L^{\alpha+2}}{\alpha+2} = + (L-1) - \frac{T_o^2}{3}(L^3-1) + \frac{T_1^{\alpha+1}}{\alpha+2} \tag{13c}$$

Equation (13c) is a new theoretical equation. The primary restrictions are those implied by Equation (2b), because only those assumptions which are easy to obtain experimentally have been invoked since that point. Thus it describes, in rather general form, the dynamic meniscus of an Ellis fluid as a function of five parameters, (T_o, T_1, C_o, C_1, and α).

PREDICTION OF DYNAMIC CURVATURE

It is not clear whether there is any need to determine the general description of the dynamic curvature from Equation (13c). At any rate, we only examine one special solution here, because our primary interest is in obtaining some analytical prediction of the influence of all the parameters. Consider the case where

$$T_1^{\frac{\alpha+1}{\alpha}} > \frac{1}{C_1}\frac{d^3L}{dR_1^3} \tag{14a}$$

If C_1 is large in the sense of Equation (14a), the α term in Equation (13c) may be expanded by the binomial theorem as follows:

$$\left[T_1^{\frac{\alpha+1}{\alpha}} + \frac{1}{C_1}\frac{d^3L}{dR_1^3}\right]^\alpha = T_1^{\alpha+1} + \frac{d^3L}{dR_1^3}\left[\frac{\alpha T_1^{\frac{\alpha^2-1}{\alpha}}}{C_1}\right] \tag{14b}$$

By substituting Equation (14b) and rearranging, Equation (13c) becomes

$$\frac{L^3}{3C_o}\frac{d^3L}{dR_1^3} = \frac{(L-1) - \frac{T_o^2}{3}(L^3-1) - \frac{T_1^{\alpha+1}}{\alpha+2}(L^{\alpha+2}-1)}{1 + T_2 \ L^{\alpha-1}} \tag{14c}$$

where

$$T_2 = \frac{3\alpha}{\alpha+2}\left(\frac{C_o}{C_1}\right) T_1^{\frac{\alpha^2-1}{\alpha}} \tag{15}$$

Equation (14c) can be further simplified by determining a solution for linear L. Thus as before (*1*, *6*), let $L = 1 + e$ where e is a small number less than unity. As a result, Equation (14c) becomes

$$\frac{L^3}{3C_o}\frac{d^3L}{dR_1^3} = \frac{e\,(1 - T_o^2 - T_1^{\alpha+1}) + O(e^2) + \ldots}{1 + T_2 + T_2(\alpha-1)\,e + O(e^2) + \ldots} \tag{16}$$

Neglecting higher order terms and $(\alpha - 1)\,e$ with respect to one, we obtain, upon returning to L

$$\frac{L^3}{3C_o}\frac{d^3L}{dR_1^3}=(L-1)\left[\frac{1-T_o^2-T_1^{\alpha+1}}{1+T_2}\right] \quad (17)$$

Now change variables by letting

$$R_2^3=\frac{3C_o\,(1-T_o^2-T_1^{\alpha+1})}{1+T_2}\cdot R_1^3 \quad (18)$$

Thus Equation (17) becomes the familiar $d^3L/dR_2^3 = (L-1)/L^3$, for which the curvature has been shown (6) to be $d^2L/dR_2^2 = 0.642$. Thus returning to R_1 by use of Equation (18), we have the following determination of the dynamic curvature:

$$\left(\frac{d^2L}{dR_1^2}\right)_D=0.642\left[\frac{3C_o\,(1-T_o^2-T_1^{\alpha+1})}{1+T_2}\right]^{2/3} \quad (19)$$

Equation (19) is also the first known use of the binomial theorem technique to withdrawal problems.

THEORETICAL PREDICTION OF FILM THICKNESS

The definition of dimensionless thickness used by Deryagin and other Russian workers (2) is

$$D_o=h_o\left(\frac{\rho g}{\sigma}\right)^{1/2} \quad (20)$$

With this definition, the previously derived static curvature is

$$\frac{d^2L}{dR_1^2}=\sqrt{2}\,D_o \quad (21)$$

The prediction of film thickness is given in explicit form by matching (19) and (21). Thus

$$h_o\left(\frac{\rho g}{\sigma}\right)^{1/2}=\frac{0.642(3)^{2/3}}{\sqrt{2}}\left[\frac{C_o\,(1-T_o^2-T_1^{\alpha+1})}{1+T_2}\right]^{2/3} \quad (22a)$$

Or

$$D_o=0.944\left\{\frac{(\alpha+2)\,C_oC_1\,(1-T_o^2-T_1^{\alpha+1})^{\frac{\alpha^2-1}{\alpha}}}{(\alpha+2)\,C_1+3\alpha C_o\,T_1}\right\}^{2/3} \quad (22b)$$

Equation (22b) is the desired solution for an Ellis fluid. Only the withdrawal speed and fluid properties are needed to evaluate film thickness h_o. It is believed that three dimensionless parameters (C_o, α, and a_1/a_0) are sufficient to evaluate Equation (22b).

With the prediction of h_o given by Equation (22a), one can predict all the other properties in the $h = h_o$ or constant thickness region. These properties include flux obtained by using Equation (5b) as well as surface velocity ($U = U_s$ at $y = h_o$) and velocity profile, both obtained by using Equations (4a) and (5b). These properties are useful for design purposes.

COMPARISON WITH PREVIOUS RESULTS

It would be natural to compare these theoretical results with data but no withdrawal data are available in Ellis model form. As noted previously (5), the data available in power law form (1) cannot be compared because no value for the low stress coefficient (a_0) has been reported. However, some comparisons can be made for special cases.

Equations (4a), (4b) and (13a), contain m. They simplify to those derived previously (1, 3) for drainage by letting $m \to \rho g$ (alternatively let σ or d^3h/dx^3 vanish). However equations involving C_o and C_1, such as Equation (22), do not readily simplify for negligible surface tension, because C_o and $C_1 \to \infty$ for this case.

Since comparison with Ellis drainage is not fruitful, we turn to power law withdrawal results. As expected, the differential Equation (13c) reduces to that previously described for the case of power law fluids. Equation (1) simplifies to a power law when $a_0 = o$, so that

$$T_o=0 \quad (23a)$$

and

$$1/C_o=0 \quad (23b)$$

Substitution of these conditions into (13c) and rearranging yield

$$\frac{1}{C_1}\frac{d^3L}{dR_1^3}=\left[\frac{(\alpha+2)(L-1)+T_1^{\alpha+1}}{L^{\alpha+2}}\right]^{1/\alpha}-T_1^{\frac{\alpha+1}{\alpha}} \quad (24a)$$

If the magnitude of the coordinate is changed as shown by Equation (24b) and the proper sign is used,* Equation (24a) becomes identical to Equation (30) of the power law reference (1).

$$R_3^3=(\alpha+2)^{1/\alpha}\,C_1\,R_1^3 \quad (24b)$$

For the special case of $a_o = o$ shown by Equations (23a) and (23b), the film thickness Equation (22b) reduces to

$$D_o=0.944\left\{\frac{(\alpha+2)\,C_1\,(1-T_1^{\alpha+1})^{\frac{\alpha^2-1}{\alpha}}}{3\alpha T_1}\right\}^{2/3} \quad (25)$$

Except for the trivial case of $\alpha = 1$ (Newtonian), Equation (25) does not agree with either of the two approximate theoretical solutions of Equation (24a) which were published previously (1). This difference is indicated by a comparison of the curvature constant of 0.642 with those other values reported for $\alpha \neq 1$ fluids (1). A detailed comparison of Equation (25) with these two unsuccessful power law solutions does not seem worthwhile.

Another possibility is a comparison of Equation (25) with the semiempirical description of the power law data (1, 5), which is

$$D_o=\left(0.41+\frac{0.25}{\alpha}\right)\left(\frac{\rho g}{\sigma}\right)^{1/2}\left[\frac{a_1^{4\alpha}\,U_w^4}{\sigma^\alpha\,(\rho g)^{3\alpha}}\right]^{\frac{1}{4+2\alpha}} \quad (26)$$

where $1 \leq \alpha \leq 3$. Equation (26) was developed by assuming that $T_1 \to 0$, which is not a suitable assumption for Equation (25). It is clear that these solutions differ.

More important than these differences is the fact that none of these power law solutions can approximate fluid behavior at low stress. A more general constitutive equation is needed for testing the theory. The best test will involve withdrawal data taken with a fluid whose constitutive properties are known to be described by the Ellis model at low and intermediate stress and whose Ellis parameters have been determined.

At this time, the most valid comparison possible is that with a low stress model (Newtonian). For this case $a_1 = 0$, so that

$$T_1=0 \quad (27a)$$

and

$$T_2=0 \quad (27b)$$

For these conditions, Equation (22a) reduces to

$$D_o=0.944\,[C_o\,(1-T_o^2)]^{2/3} \quad (28a)$$

* The power law reference (1) contains some Equations [(18) and (30)] in which the sign on the third derivative should be reversed to be consistent with the downward x axis shown in that paper (as Figure 2). However, the final curvatures and results have the proper signs.

or

$$T_o = 0.944\, C_o^{1/6}\,(1 - T_o^2)^{2/3} \quad (28b)$$

since $D_o = T_o C_o^{1/2}$ by definition. Equation (28) has been found experimentally to be valid over a 20,000-fold range of dimensionless speed C_o (6).

As compared with the theory previously developed for power model fluids, this Ellis model theory agrees with Newtonian results over a wider range of C_o. It also incorporates the behavior at low stress, as well as at intermediate stress. Therefore, it is believed that this new theory will predict the behavior of Ellis fluids. However, final verification must await suitable data.

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NOTATION

a_0, a_1 = rheological constants, Equation (1)
C_o, C_1 = dimensionless speed, Equations (11) and (12)
D_o = dimensionless thickness, Equation (20)
e = small dimensionless number
g_x, g = gravitational acceleration, cm./sec.^{2}
h = film thickness, cm.
h_o = film thickness in the constant thickness region 1, cm.
L = dimensionless coordinate, Equation (7)
m = parameter as defined by Equation (3)
P = capillary pressure, dyne/sq.cm.
Q_1, Q_2 = flux in regions 1 and 2, Equations (5b) and (4b)
R = radius of curvature, cm.
R_1, R_2, R_3 = dimensionless coordinate, Equations (8), (18), and (24b)
T_o, T_1, T_2 = dimensionless thickness, Equations (9), (10), and (15)
U = vertical fluid velocity, cm./sec.
U_s, U_w = velocity at surface and of the wall, cm./sec.
x, y = rectangular coordinates, see after Equation (2a)

Greek Letters

α = rheological exponent, Equation (1), dimensionless
ρ = fluid density, g./cc.
σ = fluid-gas surface tension, dyne/cm.
τ_{yx} = shear stress, dyne/sq.cm.

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The Use of Diagnostic Parameters for Kinetic Model Building

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In a previous paper (*1*) it was shown how an analysis of residuals of a diagnostic parameter could not only indicate the inadequacy of a proposed model for a heterogeneous chemical reaction but also could indicate *how* the model might be modified to yield a more satisfactory model. In this communication, we wish to present additional results on the exploitation of the functional form of a proposed model through the use of diagnostic parameters. The use of such a diagnostic analysis will be illustrated by *building* an adequate Hougen-Watson model from conversion-space time data on the complete vapor phase oxidation of methane over a solid palladium-alumina catalyst. The essence of the model building procedure is the analysis of the residuals of a certain diagnostic parameter occurring in the Hougen-Watson models (*2*).

The success of this technique depends to a certain extent upon the model initially considered. For instance, suppose that instead of beginning with the models of reference *1*, we had considered the grossly inadequate model

$$r = \frac{x_1(1-y)(x_2 - 2x_1y)^2}{\hat{C}_1 + \hat{C}_2 y} \quad (1)$$

where

$$\hat{C}_1 = \frac{1}{k_1K_1} + \frac{1}{k_1}x_1 + \frac{K_3}{k_1K_1}x_3 \quad (2)$$

or

$$\hat{C}_1 = b_o + b_1x_1 + b_3x_3 \quad (3)$$

and

$$\hat{C}_2 = \left(\frac{K_3}{k_1K_1} - \frac{1}{k_1}\right)x_1y \quad (4)$$

Equation (1) corresponds to the surface reaction controlled reaction of adsorbed methane with gaseous oxygen to form adsorbed carbon dioxide and vapor phase water. Hence, the expected value of the residual can be obtained by using the $\hat{C}_1$ of Equation (3) and the true value of C_1 from the previous paper (*1*):

$$C_1 = \beta_o + \beta_2x_2 + \beta_3x_3 + \beta_4x_4 + \epsilon \quad (5)$$

The expected value of the residual thus becomes

$$E(C_1 - \hat{C}_1) = E(\beta_o - b_o)$$
$$2x_1\,E(b_1) + x_2\,E(b_2) + x_3\,E(\beta_3 - b_3) + x_4\,E(b_4) \quad (6)$$

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