Hydrodynamical changes due to polymer migration in very dilute solutions *)

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Abstract: The slip hypothesis, based on thermodynamical arguments, has been extended to obtain the flow characteristics of polymer solutions flowing in a non-homogeneous flow field. An asymptotic analysis, valid for both channel and falling film flows, is presented that predicts the flow enhancement due to polymer migration. Concentration-viscosity coupling is shown to be a critical factor in the hydrodynamic analysis. The analysis, which essentially provides an upper bound on flow enhancement, explicitly accounts for the influence of wall shear stress, initial polymer concentration etc. A comparison with the pertinent experimental data shows reasonable agreement.

Key words: Slip, polymer solutions, non-uniform flow field

Notation

c	concentration
c_0	concentration in shear-free region
c_i	initial concentration
d	rate of deformation tensor
g	acceleration due to gravity
g_1	function defined in eq. [13] or [15]
g_2	function defined in eq. [18] or [20]
H	half-channel thickness or film thickness
K	gas law constant
L	length of the channel or film
q	flow rate per unit width
q^*	normalized flow rate
T	temperature
v	velocity
V	mean velocity
y	transverse distance
y_c	location of solvent layer
α	$\tau_w \lambda / \mu_s$
β	$\tau_w / c_0 KT$
$\delta/\delta t$	convected derivative
θ	dimensionless cenentration, c/c_0
θ_c	dimensionless interface concentration
θ_w	dimensionless wall concentration
λ	relaxation time
μ_{eff}	effective viscosity
μ_s	solvent viscosity
ξ	dimensionless transverse distance, y/H
ξ_c	dimensionless interface location
ρ	density

τ	stress tensor
τ_w	wall shear stress
Φ	$c_i KT / \tau_w$

Subscript

ns	no slip

1. Introduction

There is an increasing awareness now that polymeric molecules tend to migrate in non-homogeneous flow field. A number of studies which examine the causes and consequences of such phenomena have appeared in the literature over the past six years (1–8). Although the consequences of such phenomena have been increasingly appreciated [8], the mechanistic reasons are still unclear.

There appear to be four distinctly different lines of attack on this problem. Metzner et al. [1, 2] and Tirrell and Malone [3] based their arguments on the observation that in deforming fluids macromolecules stretch and align themselves thereby changing the free energy levels. Thus in a non-homogeneous flow field where there is a spatial variation of strain rate the molecular extension and orientation and consequently the free energy becomes position dependent. In order to compensate for the spatial variation in free energy levels, concentration gradients are set up. The net effect is that the macromolecules migrate towards region of low strain rate. These arguments, although intuitively appealing, have been criticised by some, since the calculation of

concentration essentially employes the application of equilib-
rium thermodynamics to non-equilibrium situations.

Aubert et al. [4, 5] have examined the problem of migratiom
in terms of the flexible bead-spring type of model of macromo-
lecules. They show that such molecules migrate relative to the
undisturbed centre of mass solvent velocity. They originally
contended [4] that even if the flow was nonhomogeneous, if it
was not a curvilinear flow, then the flexible macromolecules will
not migrate across the streamlines. However, this conclusion is
shown to be in error by Sekhon et al. [9] who clearly showed that
the inclusion of hydrodynamic interaction leads to migration
even in rectilinear flows.

The third type of models have been essentially built by Brunn
[10] and Aubert and Tirrel [11]. They showed that the presence of
wall restricts the number of configurations available to macro-
molecules near the wall thereby reducing their concentration. A
zone of concentration depletion is predicted to exist near the
wall, and rather elegant calculations have been performed by this
group with a view to examine the motion of bead-spring
mechanical models of macromolecules in the presence of a non-
penetrable interface. It is likely that this type of hydrodynamic
calculation is indeed appropriate when narrow channels are
considered. Since the order of magnitude of the wall exclusion
layer is the same as the hydrodynamic diameter of the
macromolecule, it is unlikely that such effects will be important
in larger channels.

The fourth class of models essentially relate to certain
phenomenological considerations, and incorporate slip velocity
[6–8, 12] and/or a slip layer of unknown thickness [13, 14] and
carry over the hydrodynamic or transport calculations in the
traditional way. Such calculations, although helpful from the
point of view of engineering correlations, do not throw any light
on the exact mechanistic details.

From the above it is rather evident that there are a number of
different hypotheses that have been made for examining the
phenomenon of macromolecular migration but none of these has
been proved or disproved unequivocally. Besides, it is likely that
some of these mechanisms are not essentially mutually exclusive
but might coexist. Furthermore, presently there is a large gap
between the calculations based on molecular models, the
calculations based on continuum mechanics and those which are
entirely phenomenological.

It appears that one way to sort out this important issue would
be to make alternative models or hypotheses and carry out the
calculations to their logical end. The results of the model
hypotheses could be tested against the experimentally observed
facts. It is precisely this incentive with which the present
investigation was undertaken.

We shall examine the consequence of quasi-thermo-
dynamic arguments advanced by Metzner [1] and
extended by Janssen [15] to perform some engineering

calculations on the flow enhancement in migrating
macromolecular media. This has not been attempted
before. What comes close to this work is the effort by
Tirrell and Malone [3], but there are two rather important
differences by which our work differs from theirs. The
concentration/viscosity coupling was not taken into
account by Tirrell and Malone. This will be shown to be a
very critical consideration. Secondly they did not carry
their calculations to a stage where one could have an idea
of the flow enhancement which is the primary measure-
ment invariably undertaken. Our analysis provides an *a
priori* estimate of flow enhancement due to macromole-
cular migration for dilute polymer solutions, for which
the constitutive equations used in our work are appro-
ximately valid. We find that certain very reasonable and
physically plausible observations emerge which appear to
compare at least semi-quantitatively with some of the
reported data in the literature on the flow of dilute
polymer solutions.

2. Analytical Development

We shall consider the flow of a dilute polymer solution
through a narrow channel $[L \gg H]$ as shown schemati-
cally in figure 1(a). Upon entering the channel, the
solution is subjected to a non-homogeneous deformation
field which results in the migration of the polymer from
the high shear region to low shear region near the centre.
A finite length of the channel will be required for the
migration to be complete. Therefore, we take the channel
to be sufficiently long for both the concentration and
velocity fields to be fully developed. Under these
circumstances, we are primarily interested in knowing the
detailed concentration and velocity profiles such that the
volumetric flow rate for a given wall shear stress can be
determined.

2.1. Concentration Profile

Based on the free energy expression obtained by
Marrucci [16] for a dumbell model, Metzner [2] derived
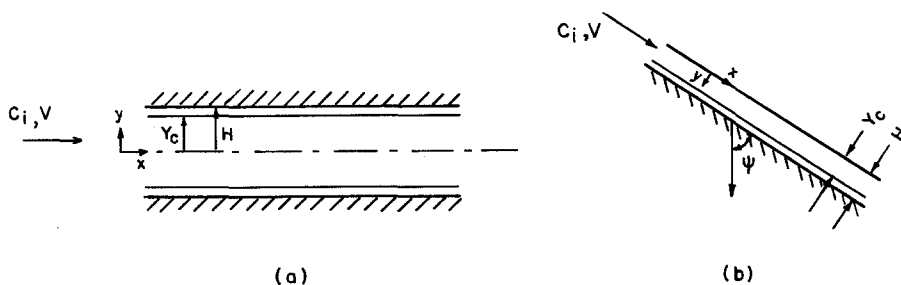the following expression for the concentration difference

Fig. 1. Schematic representation of
(a) channel and (b) falling film flow.

between regions with and without shear.

$$\frac{c_0}{c} = \exp \frac{tr\,\tau}{2cKT}.$$ (1)

Very dilute polymer solutions can adequately be represented by a Hookean dumbell model which can mathematically be descibed as

$$\tau + \lambda \frac{\delta\tau}{\delta t} = cKT\lambda.$$ (2)

Eq. (2) gives

$$tr\,\tau = 2cKT\lambda^2\,\dot\gamma^2$$

for shear flows and since the shear rate is $\dot\gamma = \tau/\mu$ eq. (1) becomes

$$\frac{c}{c_0} = \exp\left[-\left(\frac{\tau_w y}{cKTH}\right)^2\right].$$ (3)

In dimensionless terms, the concentration profile given by eq. (3) can be written as

$$\theta = \exp\left[-\left(\frac{\beta\,\xi}{\theta}\right)^2\right].$$ (4)

Eq. (4), which has been derived by Janssen [15], is an implicit equation in θ with $\theta = 0$ as its trivial solution.

Figure 2 shows some typical concentration profiles as calculated from eq. (4). It can be seen that beyond a critical value of β ($= \beta_c$), a nontrivial solution of eq. (4) exists only for a limited range of ξ. Of greater importance is the observation that within this limited range,
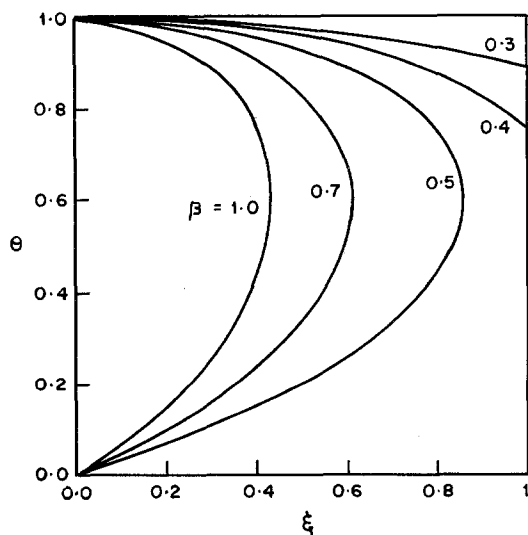

Fig. 2. Graphical representation of eq. (4)

θ is double valued as the function $\theta(\xi)$ exhibits an extremum value of θ_c at $\xi = \xi_c$. This is not physically realistic as the solution at any location cannot have two different concentrations. Since the centreline concentration, $\theta(0)$, must always be unity, the solution in the domain $1 < \theta < \theta_c$ is the only physically plausible one. Therefore for $\beta > \beta_c$, eq. (4) gives the concentration profile only for $0 \leqq \xi \leqq \xi_c$. For the remaining portion of the flow passage ($\xi_c \leqq \xi \leqq 1$), the trivial solution $\theta = 0$ must be valid. In other words, beyond a critical value of β, a pure solvent layer of thickness $1 - \xi_c$ starts forming adjacent to the wall and the bulk of the polymer slips through this low viscosity solvent layer. The above physical/mathematical arguments form the main core of our development.

The concentration gradient at the solvent layer – polymer solution interface (located at $\xi = \xi_c$) is infinite (see Fig. 2). Since

$$\xi = \frac{\theta(-\ln\theta)^{1/2}}{\beta}$$ (5)

the condition of infinite gradient implies that

$$\theta_c = \exp\left(-\tfrac{1}{2}\right) = 0.6065.$$

From eq. (5), we obtain

$$\xi_c = \frac{\theta_c(-\ln\theta_c)}{\beta} = \frac{0.4289}{\beta}.$$ (6)

Eq. [6] suggests that a pure solvent layer of thickness $1 - \xi_c$ will only be formed when $\beta > 0.4289$ ($= \beta_c$). For $\beta < \beta_c$, gradual depletion of polymer occurs from the centre to the wall and the wall concentration (θ_w) is the solution of the following transcendental equation

$$\theta_w(-\ln\theta_w)^{1/2} = \beta.$$ (7)

The preceeding discussion pertains to the situation where the viscosity depends on the polymer concentration. In the absence of such a coupling, the concentration profile is of the following form

$$\theta \propto \exp(-\xi^2)$$

as shown by Tirrell and Malone [3]. The above expression is explicit in θ and suggests a gradual depletion of the polymer. In this case, the velocity field is unaffected by the concentration redistribution and consequently the volumetric flow rate should remain unaltered. This, however, is contrary to the experimental observations thereby implying that any realistic analysis of polymer migration in non-homogeneous flow fields should incorporate a concentration dependent viscosity.

2.2. Velocity Profile

For $\beta > \beta_c$ (that is when a solvent layer is present adjacent to the wall), the velocity profile within the solvent layer can be written as

$$v = \frac{\tau_w H}{2 \mu_s} (1 - \xi^2), \quad \xi_c \leqq \xi \leqq 1 \tag{8}$$

whereas that in the polymer solution core is

$$v = \frac{\tau_w H}{2 \mu_s} (1 - \xi_c^2) + \tau_w H \int_\xi^{\xi_c} \frac{\xi \, d\xi}{\mu(\xi)}, \tag{9}$$

$$0 \leqq \xi \leqq \xi_c.$$

Taking into account the solvent contribution, the Hookean dumbell model [see eq. (2)] implies the solution viscosity (μ) to be

$$\mu = \mu_s + cKT\lambda. \tag{10}$$

Eq. (9), when combined with eq. (10) and (5), therefore becomes

$$v = \frac{\tau_w H}{2 \mu_s} + \left\{ 1 - \xi_c^2 + \frac{1}{\beta^2} \int_{\theta_c}^{\theta} \frac{\theta(2 \ln \theta + 1)}{1 + \alpha\theta/\beta} \, d\theta \right\}. \tag{11}$$

If the density change is assumed to be negligible, the total volumetric flow rate per unit width (q) can be easily obtained by integrating the velocity profile and can be expressed as

$$q = \frac{\tau_w H^2}{\mu_s} \left[\tfrac{2}{3} (1 - \xi_c^3) + g_1(\alpha, \beta) \right] \tag{12}$$

where

$$g_1(\alpha, \beta) = \frac{1}{2\beta^3} \int_{\theta_c}^{1} \frac{2 \ln \theta + 1}{(-\ln \theta)^{1/2}}$$

$$\cdot \int_{\theta_c}^{\theta} \frac{z(2 \ln z + 1)}{1 + \alpha z/\beta} \, dz \, d\theta. \tag{13}$$

For $\beta < \beta_c$, no solvent layer is present near the wall. Therefore, the velocity profile can simply be written as

$$v = \frac{\tau_w H}{2 \mu_s} \frac{1}{\beta^2} \int_{\theta_w}^{\theta} \frac{\theta(2 \ln \theta + 1)}{1 + \alpha\theta/\beta} \, d\theta \tag{14}$$

and the flow rate per unit width becomes

$$q = \frac{\tau_w H^2}{\mu_s} g_1(\alpha, \beta) \tag{15}$$

where g_1 is given by eq. (13) with θ_c replaced by θ_w.

2.3. Determination of β

Till now, the parameter β is effectively an unknown as it involves c_0, the centreline concentration. In order to solve this problem, c_0 needs to be related to the inlet concentration, c_i. For $\beta > \beta_c$, a mass balance for the polymer gives

$$q \, c_i = 2 \int_0^{y_c} vc \, dy$$

or

$$\frac{c_0}{c_i} = \frac{V}{\int_0^{\xi_c} v\theta \, d\xi} \tag{16}$$

where $V = q/2H$ is the average velocity. Eq. (16), when combined with eqs. (5) and (11), becomes

$$\frac{1}{2\beta^2} = \frac{\varphi [2/3(1 - (\beta_c/\beta)^3) + g_1(\alpha, \beta)]}{g_2(\alpha, \beta)} \tag{17}$$

where

$$g_2(\alpha, \beta) = \int_{\theta_c}^{1} \frac{\theta(2 \ln \theta + 1)}{(-\ln \theta)^{1/2}}$$

$$\cdot \left\{ 1 - \left(\frac{\beta_c}{\beta} \right)^2 + \frac{1}{\beta^2} \int_{\theta_c}^{\theta} \frac{z(2 \ln z + 1)}{1 + \alpha z/\beta} \, dz \right\} d\theta. \tag{18}$$

If $\beta < \beta_c$, the mass balance equation becomes

$$q \, c_i = 2 \int_0^{H} vc \, dy$$

and eq. (17) can be written as

$$\frac{1}{2\beta^2} = \frac{\varphi \, g_1(\alpha, \beta)}{g_2(\alpha, \beta)} \tag{19}$$

where

$$g_2(\alpha, \beta) = \frac{1}{\beta^2} \int_{\theta_w}^{1} \frac{\theta(2 \ln \theta + 1)}{(-\ln \theta)^{1/2}} \int_{\theta_w}^{\theta} \frac{z(2 \ln z + 1)}{1 + \alpha z/\beta} \, dz \, d\theta. \tag{20}$$

Eqs. (17) and (19) are both nonlinear equations implicit in β. Thus for known values of α and φ, β can be determined by numerically solving the appropriate equation. α and β, in turn, will be known if τ_w and c_i are available.

In the absence of slip (no migration), the flow rate, q_{ns}, through a plane channel can be expressed as

$$q_{ns} = \frac{2}{3} \frac{\tau_w H^2}{\mu_{ns}} \tag{21}$$

where $\mu_{ns} = \mu_s + c_i KT\lambda$. Therefore, a measure of the flow enhancement due to effective wall slip can be obtained by

considering the ratio

$$\frac{q}{q_{ns}} = \frac{\mu_{ns}}{\mu_{eff}} = \frac{3}{2} [1 + \alpha\varphi] q^* \qquad (22)$$

where $q^* = \mu_s q/\tau_w H^2$ is the normalized flow rate.

2.4. Falling film flow

An analysis, similar to that reported in the foregoing can also be used for the flow of a freely falling film down an inclined plane as shown schematically in figure 1(b). An identical procedure is to be followed and eqs. (2–14), (17–20), and eq. (22) are all valid for this flow situation, too. The only differences, arising out of the change in flow geometry, are in the expression for q and q^* which now become

$$q = \frac{\tau_w H^2}{2\mu_s} [2/3 (1 - \xi_c^3) + g_1(\alpha, \beta)] \text{ for } \beta > \beta_c, \qquad (23)$$

$$q = \frac{\tau_w H^2}{2\mu_s} g_1(\alpha, \beta) \text{ for } \beta < \beta_c \qquad (24)$$

and

$$q^* = 2\mu_s q/\tau_w H^2 \qquad (25)$$

where $\tau_w = \rho g H \cos\psi$ is the wall shear stress.

3. Results and Discussion

The preceeding analysis permits determination of the detailed flow characteristics for a given polymer concentration and wall shear stress. In the following we shall briefly discuss some of the results obtained for a typical polymeric system. In particular, we take $M = 500,000$, $T = 25\,°C$, $\lambda = 4.7 \times 10^{-4}$ sec and $\mu_s = 0.01$ poise. These values are representative of aqueous polyethylene oxide solutions at low concentrations. Before proceeding further, it needs to be emphasized that the dumbell model predicts a linear dependence of viscosity on concentration as given by eq. (10). This is true for very low concentrations; the analysis is therefore restricted to very dilute solutions. Besides, in deriving the concentration profile represented by eq. (4) the solvent contribution to the viscosity is neglected, that is $\mu \gg \mu_s$. Eq. (10) therefore implies that $\alpha \gg 1.65\,\beta$ for predictions to be meaningful.

Figure 3 illustrates the concentration and velocity profiles for a given polymer solution flowing at different rates. At low shear stresses, gradual depletion of polymer occurs from the wall to the relatively shear-free region near thr centre and the velocity profile is similar to the (no
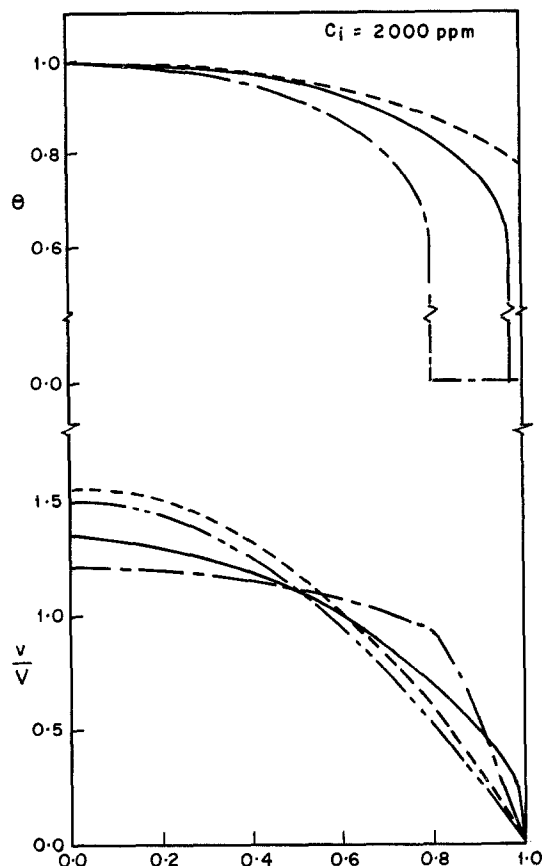

Fig. 3. Concentration and velocity profiles for a 2000 ppm solution in channel flow. Wall shear stresses were 40 (———), 46 (———), and 64 dynes/cm^2 (————); parabolic flow (———·——).

slip) parabolic shape. At higher stresses, however, the migration reaches such an extent that the wall region is devoid of any polymer and a pure solvent layer is formed adjacent to the wall with its thickness increasing as the wall shear stress increases. Correspondingly, the velocity profile within the core tends to become more uniform across the cross section. In comparison to the no-slip case, the wall shear rate is always higher in the presence of polymer migration, thereby implying effective wall slippage.

Figure 4 shows the flow enhancement ratio, q/q_{ns}, as a function of wall shear stress and the initial concentration of the polymer. Larger stresses promote increased migration which in turn is manifested as increased flow enhancement. This behaviour, however, persists only up to a certain stress beyond which flow enhancement is practically unaffected by the changes in wall shear stress. Thus, once a sufficiently thick solvent layer is formed near the wall, the migration process reaches saturation. Moreover, higher concentration implies higher elasticity
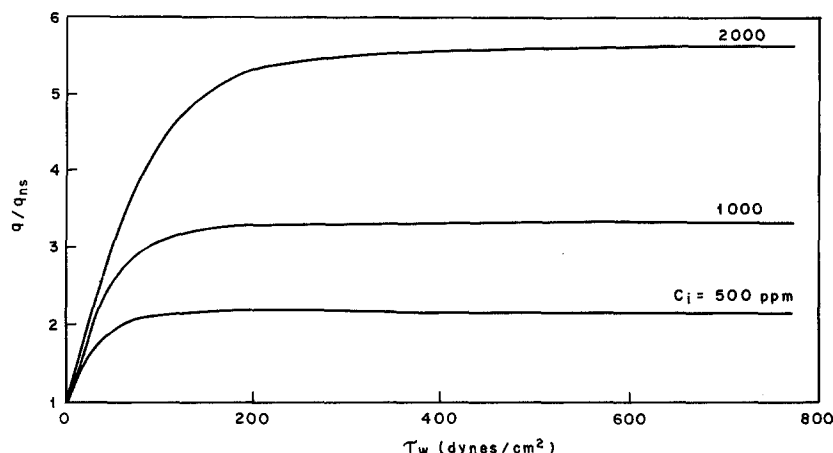
Fig. 4. Flow enhancement ratio as a function of the initial conentration of the polymer and the wall shear stress for channel flow

and therefore a larger driving force for migration at a given shear stress. Consequently, flow enhancement increases as the solution becomes more concentrated.

The results presented in Figure 4 indicate that even for very dilute polymer solutions flowing in non-homogeneous flow fields, polymer migration can cause the flow rate to be as high as five times the flow rate expected from no-slip predictions. Experimental observations by Carreau et al. [16] and Popadic [17] suggest that about 2 to 4 fold enhancement in flow rate is possible. Popadic [17] has reported falling film data for 500 ppm carbopol 934 [mol. wt. $\approx 3 \times 10^6$] solution and attributed the significant increase in flow rate to secondary flows. In an earlier work [12], we have shown that his mechanistic explanation of this "laminar drag reduction" is incorrect and have provided a phenomenological interpretation of the results. The present analysis, however, should provide a more fundamental understanding of this phenomenon. Since a 500 ppm aqueous Carbopol 934 solution is a nearly Newtonian liquid (power law index ≈ 0.95), the analysis should be applicable. A comparison between the theoretical predictions and the experimental data is shown in Fig. 5. Also shown are the corresponding no-slip calculations. Evidently, the experimentally measured flow rate for a given film thickness is always bounded by the theoretical calculations and the no-slip predictions, with the former acting as an upper bound for the flow rate. Thus not only does the theoretical analysis yield results that are comparable to experimental measurements but it also provides an upper bound on the flow enhancement. Since migration occurs by a diffusive process and diffusion coefficients of macromolecules are very low [3], extremely long lengths are likely to be necessary for full development [1]. The present theory, therefore should provide an estimation of the maximum
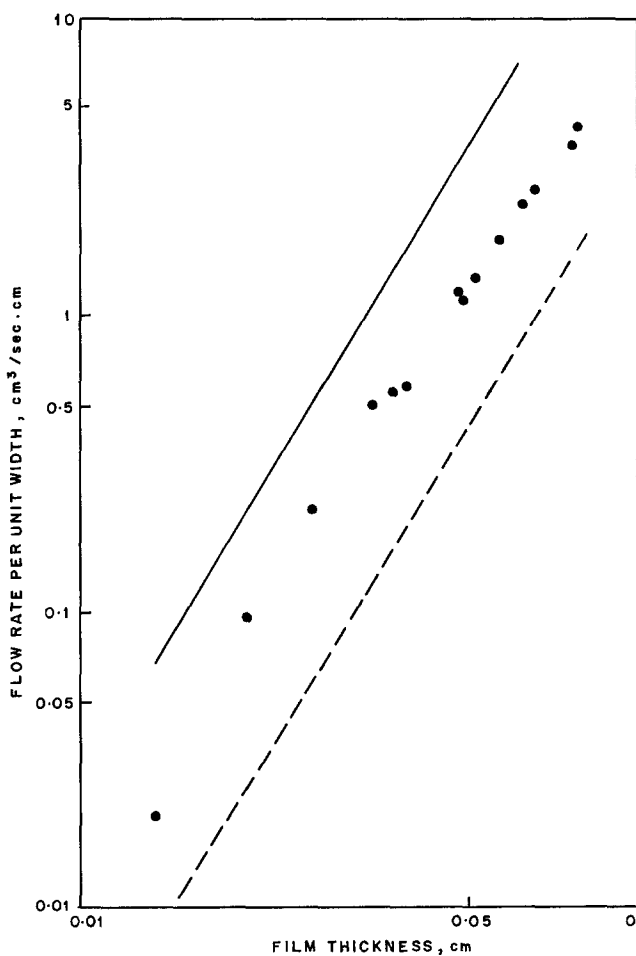

Fig. 5. Comparison of calculated results with experimental data [18] for falling film flow. Theoretical slip predictions (———), no-slip calculations (– – – – –), data for 500 ppm aqueous carbopol 934 solution (●).

amount of flow enhancement possible, or in other words, an upper bound on the flow enhancement. That this appears to be the case should act as an incentive for further theoretical development in this direction.

4. Concluding Remarks

It is worth mentioning that the analysis presented in the foregoing suffers from several drawbacks. Typically, only for very low concentration the viscosity is a linear function of concentration and hence the theory is valid only for very dilute solutions which are not of much practical interest. Besides, the Hookean dumbell model assumes a constant relaxation time independent of both shear rate and concentration. Undoubtedly, this is a rather poor approximation. Finally, the existence of a Fickean diffusion flux opposing the migration effect is not accounted for in the analysis and therefore, the theory is expected to over-predict the flow enhancement.

Surprisingly, inspite of these serious shortcomings, the theoretical predictions are not only comparable to experimental observations but also provide an upper bound on the flow enhancement. At the present state of development, this is indeed quite encouraging and should provide impetus for further work. Particularly, analyses incorporating more realistic fluid behaviour and describing the developing stage of macromolecular concentration field will decidedly be rewarding in understanding the origin of macromolecular migration in non-homogeneous flow fields.

References

1. Metzner, A.B., in: Shah, D.O. and R.S. Schechter, [eds.] Improved Oil Recovery by Surfactant and Polymer Flooding, Academic Press (New York 1977).
2. Metzner, A.B., Y. Cohen, C. Rangel-Nafaile, J. Non-Newtonian Fluid Mech. 5, 449 (1979).
3. Tirrell, M., M.F. Malone, J. Polym. Sci. 15, 1569 (1977).
4. Aubert, J.H., M. Tirrell, J. Chem. Phys. 72, 2694 (1980).
5. Aubert, J.H., S. Prager, M. Tirrell, J. Chem. Phys. 73, 4103 (1980).
6. Dutta, A., R.A. Mashelkar, Rheol. Acta 21, 52 (1982).
7. Dutta, A., R.A. Mashelkar, J. Appl. Polym. Sci. 27, 2739 (1982).
8. Mashelkar, R.A., A. Dutta, Chem. Eng. Sci. 37, 969 (1982).
9. Sekhon, G., R.C. Armstrong, M.S. Jhon, J. Polym. Sci., Polym. Phys. Ed. 20, 947 (1982).
10. Brunn, P., Rheol. Acta 15, 23 (1976).
11. Aubert, J.H., M. Tirrell, Polym. Preprints 33, 82 (1981).
12. Dutta, A., R.A. Mashelkar, Amer. Inst. Chem. Eng. J., in press.
13. Kozicki, W., S.N. Pasani, A.R.K. Rao, C. Tiu, Chem. Eng. Sci. 25, 41 (1970).
14. Chauveteau, G., J. Rheol. 26, 111 (1982).
15. Janssen, L.P.B.M., Rheol. Acta 19, 32 (1980).
16. Marrucci, G., Trans. Soc. Rheol. 16, 321 (1972).
17. Carreau, P., Q.H. Bui, P. Leroux, Rheol. Acta 18, 600 (1979).
18. Popadic, V.O., Amer. Inst. Chem. Eng. J. 21, 610 (1975).

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