Sobretiro de

ADVANCES
IN RHEOLOGY

VOLUME 2: FLUIDS

Proc. IX Intl. Congress on Rheology, Mexico, 1984.

ADSORPTION AND APPARENT SLIP EFFECTS IN THE FLOW OF POLYMER SOLUTIONS AND MICROEMULSIONS THROUGH POROUS MEDIA

Yoram Cohen
Department of Chemical Engineering
University of California, Los Angeles
Los Angeles, California 90024

ABSTRACT

Polymer solutions and microemulsions are shown to exhibit abnormal flow enhancement, termed here apparent slip, when flowing through porous media. In contrast, polymer adsorption at the pore walls can result in significant flow reduction.

An experimental investigation of the above phenomena is reported for aqueous polymer solutions, and for oil-in-water microemulsions in porous media and capillary tubes. The results of this study provide a procedure for the separation and quantification of apparent slip, adsorption, and viscoelastic effects.

INTRODUCTION

The flow behavior of both microemulsions and polymer solutions through porous media has been extensively studied in the literature with the specific goal of modeling the pressure drop-flow rate relationship for these fluids. Extensive reviews of the complex flow behavior of polymer solutions in porous media have been provided by Savins (1969), Metzner (1977), Willhite and Dominguez (1977), Wang et al. (1979), and Dreher and Gogarty (1969). Detailed accounts of the flow behavior of microemulsions in porous media have been reported by Gogarty (1867), Sheffield and Metzner (1976), Uzoigwe and Marsden (1970), Alvarado and Marsden (1979), and Cohen and Cheng-Nian (1984). In both the flow of microemulsions and polymer solutions, "anomalous" behavior associated with the wall region in the porous medium channels may lead to either a flow enhancement or retardation (Savins, 1969; Kozicki et al., 1967).

Polymer adsorption onto the pore walls may lead to significant permeability reduction as well as a loss of the polymeric additive. Adsorption effects however, are usually accompanied by other complex phenomena such as hydrodynamic polymer retention (Maerker, 1973; Chauveteau and Kohler (1974) and viscoelastic effects (Marshall and Metzner, 1967) both which contribute to permeability reduction. These complications to date, have complicated the separation and quantification of adsorption from other competing phenomena. The existing studies have generally quantified the resistance of a residual adsorbed polymer layer to the flow of the solvent and not the desired resistance to the flow of the polymer solution.

Abnormal flow enhancement may occur for both polymer solutions and emulsions. Such an effect is known as apparent slip (Cohen and Metzner, 1982,1984) and it is normally associated with the formation of a thin wall layer depleted of polymer or emulsion droplets. The apparent slip phenomenon has been recently reviewed for capillary tube flow of polymer solutions (Cohen and Metzner, 1984; Chauveteau, 1982) and microemulsions (Cohen and Cheng-Nian, 1984). The corresponding phenomenon in porous media flow has not been well appreciated in the literature due to the difficulty in separating the various complicating phenomena (Cohen and Christ, 1984). It is important to note that such effects may lead mobility enhancement and hence possible fingering that is undesirable in oil recovery operations. In the case of polymer solutions. apparent slip or mobility enhancement are most significant in small pores (Cohen and Metzner, 1982). Consequently, apparent slip flow may counteract the reduction in mobility due to adsorption and elastic effects and thereby contribute to equalizing the frontal velocity of the injected polymer slug.

ANALYSIS

The Newtonian shear rate-shear stress relationship for capillary tube flow can be expressed by (Mooney, 1931)

$$\dot{\gamma}_{ac} = 8\langle V\rangle/D = BV_m/D + \frac{4}{\tau_w^3}\int_0^{\tau_w} \tau^2 f(\tau)d\tau \qquad (1)$$

in which D is the tube diameter, <V> is the average velocity, V_s is the effective slip velocity at the tube wall, τ_w is the wall shear stress, τ is the local stress, and $f(\tau)$ is the corresponding shear rate function.

A parallel analysis for porous media flow yields (Kozicki et al., 1967; Savins, 1969),

$$\dot{\gamma}_{ap} = 8\langle V\rangle/(4R_H) = 8V_{sp}/4R_H + \frac{4}{\tau_{wp}^3}\int_0^{\tau_{wp}} \tau^2 f(\tau)d\tau \qquad (2)$$

in which <V> is the interstitial velocity that is replaced by $V_o(Le/L)/\varepsilon$, where V_o is the superficial velocity and ε is the bed porosity (Kemblowski and Michniewicz, 1979). The wall stress in the packed bed τ_{wp} is given by

$$\tau_{wp} = \Delta P/[(Le/L)(L/R_H)] \qquad (3)$$

where Le/L is the tortuosity factor taken as 1.443 for polydisperse spheres (Cohen and Metzner, 1981). Finally, the hydraulic radius R_H, is defined as $R_H = D_p\varepsilon/[6(1-\varepsilon)]$ (Bird et al., 1960) where D_p is the particle diameter. Equation (2) is an equivalent form of the capillary-power law model (CPL) if the stress is expressed by the power law model namely, $\tau = K\dot{\gamma}^n$ (K and n are the power law parameters).

In the presence of adsorption, the flow retardation can be expressed by an effective hydrodynamic thickness of the adsorbed polymer layer,

$$\delta = 2R_H[1-(\dot{\gamma}_{ad}/\dot{\gamma}_{ap})^{n/(3n+1)}] \qquad (4)$$

in which $\dot{\gamma}_{ad}$ and $\dot{\gamma}_{ap}$ are the Newtonian shear rates in the presence and absence of an adsorbed polymer layer, respectively.

EXPERIMENTAL

The flow experiments consisted of determining the pressure drop-flow rate relationship for the flow of aqueous solutions of partially hydrolyzed polyacrylamide (Separan AP-30 and J333, Dow Chemical Company) and water-in-oil microemulsions through packed beds of silica sand (Agsco Corporation, Paterson, NJ) and single stainless steel capillary tubes. The microemulsions used in this study all had the following similar composition by volume percent; 3% distilled water, 1% isopropyl alcohol, 76.5% isooctane, ad 19.5% sodium sulfonate. Significant apparent slip effects were previously shown to exist for lower surfactant concentrations and higher water-to-oil ratios (Cohen and Cheng-Nian, 1984).

The packed bed and single capillary experiments were carried out using a stainless steel constant pressure rheometer (Christ, 1984). All of the equipment parts in contact with the test fluid were manufactured from stainless steel. Temperature control (23 ± 0.5) was achieved by circulating water from a constant temperature water bath through a water jacket around the apparatus. The packed bed made of Lucide, was 20.3 cm long and 1.3 cm in inside diameter. The column to particle diameter ratio, D_c/D_p, was approximately 140 for the packed beds studied in this work, hence column wall effects were negligible (Cohen and Metzner, 1981). The pressure drop across the packed bed was measured using a stainless steel differential pressure transducer with interchangeable diaphragms (Model DP15, Validyne Engineering, Northridge, CA). The pressure transducers were calibrated periodically using a dead-weight tester (Model T-10, Amatek Mansfield and Green, Sellersville, PA) with an accuracy of 0.1% of the calibrated pressure. The overall error in the pressure drop measurements was estimated to be less than ±0.1%. The pressure was controlled to ±0.02 psi during each flow rate determination. Flow rates were determined by using an electronic load cell of a design similar to that of Cohen (1981). The estimated error in the flow measurements was less than ±0.5%.

The flow experiments were all carried out in both adsorbing and non-adsorbing packed beds, and single capillaries. Non-adsorbing surfaces were prepared by chemically treating the packed silica beds and the capillary tubes with a solution of 2% dimethyldiethoxysilane in a solvent mixture made of 95% ethanol and 5% distilled water, adjusted to a pH of about 4.5-5.5 with acetic acid. Details of the treatment procedure are described elsewhere (Cohen and Christ, 1984; Cohen, 1983). The adsorbing surfaces were the native untreated surfaces onto which the various polymers were adsorbed from either stagnant or flowing polymer solutions.

RESULTS AND DISCUSSION

The evaluation of adsorption and apparent slip effects has been based on the simple capillary-power law (CPL) model since the main interest on this work was to assess the relative magnitude of these two effects. In the initial part of the study it was demonstrated that the CPL model accurately describes the pressure drop-flow rate behavior of inelastic shear thinning microemulsions for which both adsorption and apparent slip effects are absent. The results for such a fluid are shown in Fig. 1. The capillary flow curves are equivalent to the prediction of the CPL model (Eq. 2). The average error in the prediction of Eq. (2) is about 6%. Previous studies have tested the CPL model for either viscoelastic polymer solutions (Christopher and Middleman, 1965; Savins, 1969, Duda et al., 1980) and emulsions for which significant <ins>apparent</ins> <ins>slip</ins> effect were present (Sheffield and Metzner, 1976; Cohen and Cheng-Nian, 1984). Moreover, the comparison has often been made based on a friction factor-Reynolds number correlation that obscured the actual errors in the prediction (Sheffield and Metzner, 1976).

The results depicted in Fig. 1 suggest that experimental flow rates that are less than the CPL prediction can be attributed to elongational flow, in the absence of adsorption, as originally suggested by Marshall and Metzner (1967). Flow rates higher than the CPL model prediction can be attributed to <ins>apparent</ins> <ins>slip</ins> from (Cohen and Cheng-Nian, 1984). The test for the presence of both viscoelastic and <ins>apparent</ins> <ins>slip</ins> flow in porous media can then be accomplished by plotting the ratio of the experimental to predicted shear rates γ_{ex}/γ_{pr}, versus the Deborah number. The Deborah number, De, for porous media flow can be defined by De = $\theta \langle V \rangle / D_p$ in which θ is the Maxwell relaxation time (Marshall and Metzner, 1967). The correlation of γ_{ex}/γ_{pr} versus De, for two polyacrylamide solutions (Separan AP-30) is shown in Fig. 2. The results indicate that at a De number greater than about 0.08, the experimental flow rates are lower than predicted by Eq. (2). This "critical" De number marks the "onset" of viscoelastic effects. This is in agreement with the results of Marshall and Metzner (1967) if the factor of Le/L is included in their definition of the De number (Kemblowski and Michniewicz, 1979). Below a De number of about 0.08, the experimental flow rates are higher than the CPL model prediction. This flow enhancement is the consequence of <ins>apparent</ins> <ins>slip</ins> effects that become significant at low De numbers versus viscoelastic effects diminish. It is worth noting that in enhanced oil recovery operations the value of De may be significantly lower than unity. This suggests that at the low De

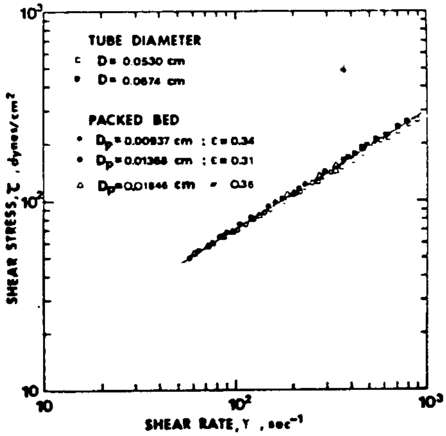

Fig. 1. Flow Curves for Water-in-Oil Microemulsions

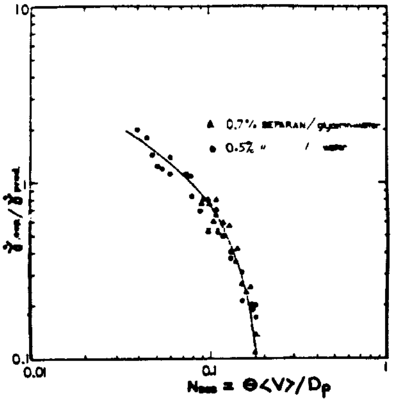

Fig. 2. Correlation of Measured to Predicted Shear Rates (Eq. 2) for Separan Solutions in Porous Media

region apparent slip effects may be of particular importance in oil recovery operations. This of course provided that adsorption effects are negligible.

In contrast to apparent slip flow, polymer adsorption onto the channel walls leads to flow reduction. The flow curves for J333 polymer in adsorbing and non-adsorbing silica sand beds and in a non-adsorbing capillary tube are given in Fig. 3. These results clearly indicate that the Newtonian shear rate at a given stress level is lower for the native adsorbing surfaces. This flow retardation is due to the presence of an adsorbed polymer layer. Additionally, the stress levels in the packed beds are substantially higher than in the capillary rheometer at the same shear rate. This additional resistance to flow in the packed beds is due to viscoelastic effects.

The flow retardation due to adsorption can be more conveniently expressed as an effective hydrodynamic thickness (EHT) of the adsorbed polymer layer. The EHT values for two different silica beds are shown in Fig. 4. The EHT decreases with increasing shear stress level due to the deformation of the adsorbed polymer layer. These results are in qualitative agreement with the EHT values reported by Cohen and Metzner (1982) for capillary tube flow. The results depicted in Fig. 4 translate to a permeability reduction that increases with a decreasing stress level. Such a behavior was reported earlier by Fan (1989), Duda et al. (1980), and Wang et al. (1979) for a pure solvent flowing over a residual adsorbed layer. It is emphasized that the current results, in contrast to previous studies, depict the resistance of the adsorbed polymer layer to the flow of the polymer solution. Hence the present results are a more accurate representation of permeability reduction due to polymer adsorption.

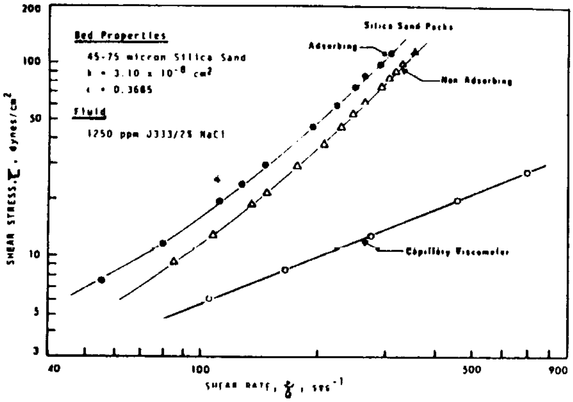

Fig. 3 Flow Curves for 45-75 Micron Silica Sand

The largest EHT values determined in this study were about 0.9 μm at a shear rate level of 55 sec^{-1}. This is about three times the magnitude of the residual EHT reported by Thomas (1976) for an equivalent polyacrylamide (Pusher 700) in a capillary tube flow. It is interesting to note that the lowest shear rate level in Fig. 4 corresponds to a frontal velocity of about 18 ft/day which is higher than the typical frontal velocities encountered in enhanced oil recovery operations. Therefore, it is speculated that at shear rate levels lower than achieved in this study, the EHT and hence the permeability reduction may be even greater.

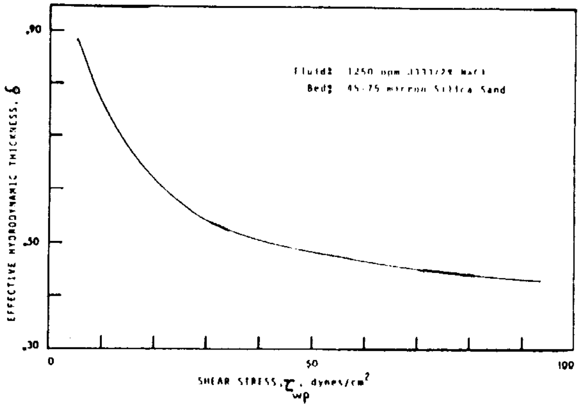

Fig. 4. Effective Hydrodynamic Thickness (EHT) for 45-75 Micron Silica Sand Packs

The results of this study have demonstrated that both apparent slip flow and flow retardation due to polymer adsorption are significant in porous media flow of polymer solutions, particularly at low shear rate (or stress levels). Consequently these phenomena may be of importance in enhanced oil recovery operations where the shear rate levels are even lower than investigated in the present study. The flow reduction due to adsorbed polyacrylamide was found to be as high as 20%. This reduction is significant at low stress levels but it is masked by dominant viscoelastic effects at high shear rates. In contrast, apparent slip effects may lead to a significant flow enhancement (as high as 100%) for non-dilute polymer solutions in the absence of adsorption (Fig. 2). Previous work in capillary tube flow (Cohen and Metzner, 1984) indicated negligible apparent slip effects for polyacrylamide concentrations which were below 0.1%. Therefore, it is suggested that at low concentrations and low shear rates flow retardation due to adsorption is more significant than either viscoelastic or apparent slip effects.

The experimental method of this study allowed the direct comparison of the flow behavior of adsorbing and non-adsorbing surfaces. This method is currently being extended to the analysis of adsorption effects in actual reservoir core samples.

REFERENCES

Alvarado, D. A., and S. S. Marsden, Jr., Soc. Pet. Engrs. AIME J., 19, 369 (1979).

Chauveteau, G., and N. Kohler, Paper SPE No. 4745, Oil Recovery Symposium of SPE-AIME, Tulsa, OK (1974).

Chauveteau, G., J. Rheology, 26, 111 (1982).

Christopher, R. H., and S. Middleman, Ind. and Eng. Chem. Fund., 4, 422 (1965).

Cohen, Y., and A. B. Metzner, AIChE J., 27, 705 (1981).

Cohen, Y., and A. B. Metzner, Macromolecules, 15, 1425 (1982).

Cohen, Y., and A. B. Metzner, AIChE Symp. Series, 78, 77 (1982).

Christ, F. R., "Hydrodynamic Adsorption Effects in the Flow of Polyacrylamide Solutions Through Porous Media", M.S. Thesis, University of California, Los Angeles, CA (1983).

Cohen, Y., and A. B. Metzner, J. Rheology, in press (1984).

Cohen, Y., and C. Cheng-Nian, Chem. Eng. Communications, in press (1984).

Cohen, Y., and F. R. Christ, Soc. Pet. Engrs. J., submitted for publication (1984).

Dreher, K. D., and W. B. Gogarty, J. Rheology, 23, 109 (1979).

Duda, J. L., E. E. Klaus and S. K. Fan, Paper SPE No. 9298, 55th Annual SPE Meeting, Dallas, TX (1980).

Fan, S. K., M.S. Thesis, Pennsylvania State University (1980).

Gogarty, W. B., Trans. Soc. Pet. Eng., 240, 149 (1967).

Kozicki, W., C. J. Hsu, and C. Tiu, Chem. Eng. J., 22, 487 (1967).

Kemblowski, Z., and M. Michniewicz, Rheologica Acta, 18, 730 (1979).

Maerker, J. M., J. Petrol. Technol., 25, 1307 (1973).

Marshall, R. J., and A. B. Metzner, Ind. and Eng. Chem. Fund., 6, 393 (1967).

Metzner, A. B., in "Improved Oil Recovery by Surfactant and Polymer Flooding", D. O. shah and R. S. Schechter (eds.), Academic Press Inc. (1977).

Mooney, M., J. Rheology, 2, 210 (1931).

Sheffield, R. E., and A. B. Metzner, AIChE J., 22, 736 (1976).

Savins, J., Ind. and Eng. Chem., 61, 18 (1969).

Thomas, C. P., Soc. Pet. Eng. J., 16, 139 (1976).

Uzoigwe, A. C., and S. S. Marsden, Jr., SPE paper No. 3004, SPE-AIME 45th Annual Fall Meeting, Houston, Oct. 4-7 (1970).

Wang, F. H. L., J. L. Duda, E. E. Klaus, S. K. Fan and S. J. Ju, Soc. Pet. Eng., paper No. 8418 (1979).

Willhite, G. P., and J. G. Diminguez, in D. O. Shah and R. B. Schechter (eds.), Improved Oil Recovery by Surfactant and Polymer Flooding, Academic Press, NY (1977).