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Wetting Kinetics of Polymer Solutions. Experimental Observations

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ABSTRACT: It is known that the spreading rates of small liquid drops over a solid surface exhibit a strong dependence on the viscosity of the liquid. These observations have led us to study the spreading behavior of polymer solutions on high- and low-energy substrates to determine what role complex rheology plays in wetting kinetics. We did not observe any effects of non-Newtonian (nonlinear) behavior, nor were any obvious signs of viscoelasticity (memory) visible. Instead, we observed a most intriguing phenomenon that polymer solutions, despite having low surface energies, do not wet high-energy substrates. In addition, nonwetting drops spread to an equilibrium configuration by either one of two distinct mechanisms. In the first case, they spread as a wetting Newtonian liquid and then stopped, that is, equilibrated, abruptly. In the second, they equilibrated continuously. We offer some possible molecular and continuum arguments to explain the differences between these two mechanisms.

Introduction

The rate at which a small drop spreads on a solid surface is the wetting or spreading kinetics, an area that has been researched extensively and reviewed in detail.[1−7] The type of problem that the spreading of the drops falls under is that of spontaneous wetting. This phenomenon has received much attention because of a large number of applications[4] and because of some problems of a fundamental nature that arise while quantifying the phenomenon. The fluid mechanical treatments show that the stresses become infinite at the contact line, the line common to the moving liquid, the solid substrate, and the fluid (usually air) that is being displaced. These unbound stresses have led to theories about what actually may be happening at the contact line, while keeping the continuum hypothesis intact.[8,9] However, one also observes that the continuum hypothesis does break down near the contact line, and new phenomena have been observed at that level.[10] At a macroscopic level, the dynamic contact angle, θ (Figure 1), is seen to be different from its value at equilibrium, leading to the possibility that a local equilibrium is not valid at the contact line, even though it appears to hold everywhere else in the system.

One other interesting observation is that the drop shapes are those of spherical caps. Finer details very close to the contact line show significant deviations. In terms of fluid mechanics, these deviations imply that the driving force in the drop is confined to this small region near the contact line. Several ideas have been established by researchers in the area of wetting kinetics. First, it is necessary to postulate a slip boundary condition at the contact line. This eliminates the unbound behavior and even provides the expression for the rate of wetting in spontaneous spreading, which is impossible to obtain without using a slip condition.[8,9] Second, one can postulate many slip conditions, but within a class it is not possible to distinguish clearly one slip condition from another.[11] Third, on smooth surfaces, details have been discovered on molecular scales that have yet to be quantified,[7,10] and their impact on spreading kinetics is as yet unknown. Finally, researchers agree that the dynamic contact angle is most likely an artifact due to a lack of resolution in the visual observations.[8,20] The actual angle during spreading is probably the equilibrium contact angle.

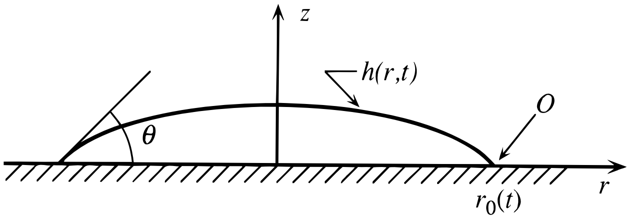

Figure 1. Profile of a moving drop (spherical cap). The contact line is at r_o, and the apparent dynamic contact angle is θ. The precursor film, where it exists, is not seen at this scale.

The importance of viscous forces in the vicinity of the contact line appears to be widely accepted. However, a curious fact is that no distinction is made between a Newtonian fluid and a non-Newtonian fluid. Kwei et al.[12] reported the earliest data on the spreading kinetics of drops, which show that polymer melts (non-Newtonian) and glycerol (Newtonian) display the same quantitative behaviors, using only nominal values for the melt viscosity. Chen[13] and Cazabat et al.[14] have provided very detailed data for poly(dimethylsiloxane), a molten polymer. Again, the results for what should be a non-Newtonian fluid agree quite well with the newer data for Newtonian liquids.[15] These data deal with wetting liquids, and the results for a single fluid can be described by[8,16,17]

$$r_o/V^{1/3} = a(c + t/V^{1/3})^{1/10} \tag{1}$$

where r_o is the basal radius (Figure 1), V is the drop volume, which is sufficiently small such that the gravity can be neglected, t is the time, and a and c are constants, where c is related to the initial condition. The constant a contains viscosity and surface tension, and at large times,

$$r_o/V^{1/3} \sim a[t/V^{1/3}]^{1/10} \tag{2}$$

which upon rearrangement yields

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$$\frac{r_o}{V^{1/3}} \propto Ca^{-1/10} \tag{3}$$

Here, the capillary number $Ca = \mu(V^{1/3}/t)/\gamma$.

Very little data exist on the spreading kinetics of nonwetting liquids. Van Oene et al.[18] have reported data on drops for systems that have very large contact angles. Van Remoortere and Joos[19] have reported extensive data on climbing films. One key feature in their observations is that the value of the equilibrium contact angle, λ, is needed to explain the data on the dynamics. In contrast, Zosel[15] observed that a nonwetting fluid spread at the same rate as a wetting fluid, but after some time, the fluid drop abruptly equilibrated. That is, the rate was unaffected by the equilibrium contact angle. Van Remoortere and Joos used pure liquids like paraffin oils on silane or paraffin-coated tubes where the contact angles tended to be high, reaching 40°. The nonwetting liquid used by Zosel was a solution of poly(isobutylene) (MW 280 000) in decalin on PTFE, which had much lower contact angles.

In effect, there are two features in this study of wetting kinetics that represent the broad issues. These are the following: (1) the effects of non-Newtonian rheological properties. These involve both nonlinear shear stress−shear rate relations and viscoelasticity and are investigated here by using polymer solutions. (2) The effect of a lack of wetting is another feature. Two types of behaviors have been documented by Zosel and by van Remoortere and Joos. Consequently, one not only needs a description of the spreading rates for nonwetting liquids but one also needs a resolution of the preceding conflict. As it turns out, polymer solutions are nonwetting with small contact angles, thus permitting investigation of both features.

Described herein are the experiments performed to measure the wetting kinetics of small drops of polymer solutions. The nominal drop sizes of 10 μL were produced by using a micrometer syringe on the substrate placed on the stage of Ramé-Hart goniometer. The dynamic contact angle θ and r_o were measured as functions of time. Instead of reading the values of r_o and θ at different times, changes in r_o were preset and the time to reach that value and its corresponding θ was recorded.

Experimental Section

Dibutyl phthalate (DBP) and squalane were used as purchased (Aldrich) at a purity of 99.8% or better. Polystyrene of average molecular weights 45 000 (Scientific Polymer Products) and 280 000 (Aldrich) were used. Poly(dimethylsiloxane) of molecular weight 17 000 was purchased from Polysciences.

The polymer solution used throughout was polystyrene in DBP. Polystyrene could be dissolved in DBP only by heating the mixture to 90 °C. Upon cooling, a clear solution resulted over the concentration ranges used here and even beyond the highest concentration used, which was 40 wt %. DBP is very nonvolatile, with a boiling point of 350 °C, and thus very suitable for the present studies.

The substrates chosen were glass (biological slides) and, in a few cases, commercial grade poly(methyl methacrylate) (PMMA). The glass was cleaned by first boiling in 70% nitric acid then immersing in KOH−propanol solution and finally in hot 1% EDTA (ethylenediaminetetraacetic acid, tetrasodium salt hydrate, Aldrich). In between, the glass was cleaned in double-distilled water and finally in deionized water, which was seen to be wetting. DBP also wets this glass. PMMA sheets could be cleaned with methanol to the point that DBP wets PMMA.

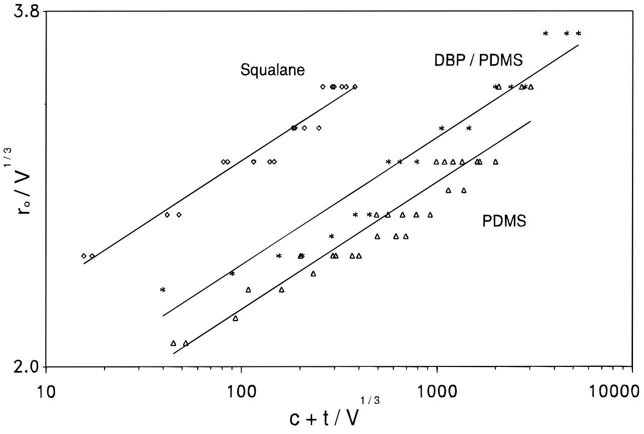

Figure 2. Extent of wetting expressed as in eq 1 for squalane, 25% DBP-in-PDMS, and PDMS on glass; all liquids are wetting.

By using the procedure described earlier, both r_o and θ were measured with time. If one assumes that the drop shape is described by a spherical cap, then the drop volumes can be calculated from

$$V = \frac{\pi(1 - \cos\theta)(2 + \cos\theta){r_o}^3}{(3\sin\theta)(1 + \cos\theta)} \tag{4}$$

Although the drop volumes varied slightly from run to run, the calculated volumes remained constant over time within runs, thus verifying both the spherical drop assumption and the constant volume assumption. The system was allowed to stand for at least 24 h before the equilibrium contact angle was measured. After equilibration, the contact line region was examined under microscope. All experiments were done at room temperature.

The goniometer has a least count of 1° and 0.2 mm in linear displacements.

Results

The results of poly(dimethylsiloxane) (PDMS), DBP-in-PDMS emulsion with 25% DBP, and squalane on glass are shown in Figure 2. We made three runs using pure PDMS: one with the DBP-in-PDMS emulsion and two with squalane. For every run, an average value of V was calculated by using eq 4. By using this value, nonlinear regression was used to evaluate the constants a and c (see eq 1). As mentioned earlier, c depends on initial conditions and varied from run to run, but a remained relatively constant. The mean (where applicable) value of a was used to draw the fitted plots in Figure 2. It is noteworthy that this is the only parameter needed to make those plots.

Because remarks have been made elsewhere regarding the validity of the power 1/10 in eq 1, we also performed a parameter estimation by allowing the power to float as the parameter ν. The curve fit improved, with ν ranging from 0.06 to 0.14, if one looked only at the decreased value of the residual sum of squares (RSS). However, the number of degrees of freedom when ν is fixed at 1/10 is $N - 2$, where N represents the number of data points and 2 represents the number of parameters. When ν is a variable, the number of degrees of freedom becomes $N - 3$. One should make a statistical inference on the basis of RSS *per degree of freedom*,[21] and when this number was calculated, it was seen that, for every case shown in Figure 2, RSS per degree of freedom was less when ν was fixed beforehand at 1/10.

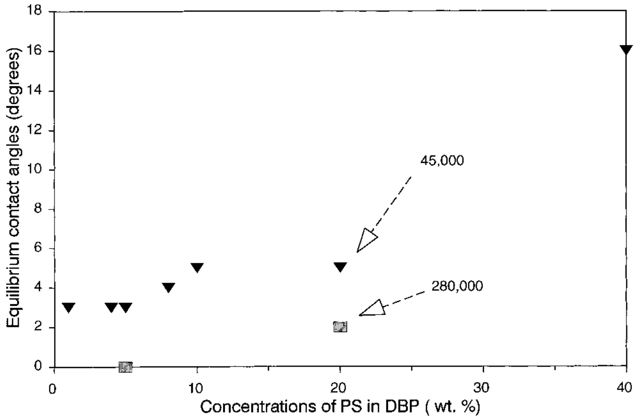

Figure 3. Equilibrium contact angles on glass shown as a function of polymer concentration in DBP.

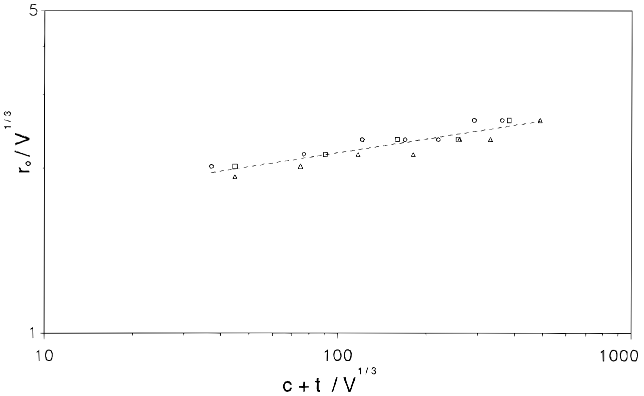

Figure 4. Extent of wetting of 5% polystyrene in DBP on glass. Three runs are shown. They show different values of constant *c*, as defined in eq 1, but almost the same value of *a*.

The data for PDMS and the DBP-in-PDMS emulsion in Figure 2 were taken over glass cleaned only with a detergent solution. PDMS wet the substrate, but DBP did not. It is interesting to note that the 25% emulsion also showed the characteristics of a wetting liquid. The emulsion drop sizes were not measured, but the milky white emulsion was prepared with a biohomogenizer, and drops could well have been in the micrometer-to-submicrometer domain. For squalane the glass was subjected to the special cleaning procedure described earlier. The key feature in Figure 2 is that the Newtonian fluid, represented by squalane, spread no differently from the non-Newtonian PDMS.

All substrates used in the experiments described here were cleaned using the prescribed procedure. To our great surprise, polystyrene solution in DBP did not wet clean glass, even though DBP alone did. The accuracy of measurements at these low values of contact angles is not very good. The results are shown in Figure 3. The high molecular weight polystyrene showed a different behavior. DBP has a surface tension of 33.4 mN/m, and polystyrene has a critical surface tension of 33–35 mN/m; there is no simple reason why the solution should be nonwetting.

In Figure 4, the results are shown for three runs with 5% polystyrene (MW 45 000) in DBP on clean glass. The kinetic data for solutions below 5% could not be taken because they spread too rapidly for the present methods of measurement. In addition, the contact lines were unstable, showing scalloped edges. This was particularly true for the 1% solution. The scatter in data, as seen in Figure 4, decreased with increasing polymer concentrations, as the viscosity increased and decreased the spreading rates. In Figure 5, the kinetic data for all concentrations studied are shown. Only fitted lines are shown up to 20% polystyrene. The substrate is clean glass, and the polystyrene molecular weight is 45 000. The plots in Figure 5 that end abruptly do so because the drops did not spread any further, that is, they suddenly equilibrated, a feature also observed by Zosel[15] for a polymer solution. In contrast to Zosel-type behavior, the 40% solution showed Joos-type behavior,[19] where the system equilibrated continuously. According to Figure 3, it is also the system that has, comparatively speaking, a much larger equilibrium contact angle. Except for this last case, all data fit eq 1, where in general the contribution of the *c* term was found to be small and has been dropped from Figure 4 onward.

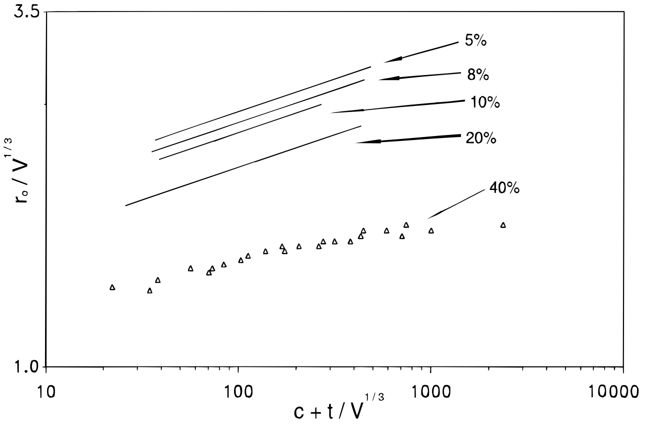

Figure 5. Extent of wetting of polystyrene in DBP on glass. Different values of polymer concentration are shown in the figure. The kinetics follow eq 1 up to 20% polymer concentration. Only fitted lines are shown. The data points are for 40% polymer, which obviously follows a different rule and, in addition, equilibrates continuously. The systems at lower concentrations all equilibrate suddenly at the end of the curves shown.

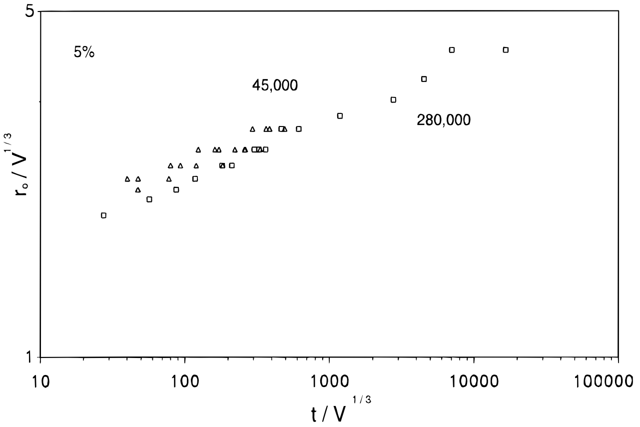

Figure 6. Comparison between 5% polystyrene of molecular weights 45 000 (three runs) and 280 000 (one run) on glass. The second fluid is wetting.

Because of the differences in the behavior in the equilibrium contact angles with the molecular weights of the polymer (Figure 3), the spreading rates were also studied as a function of molecular weight. Figure 6 compares the spreading rates of 5% polystyrene of molecular weight 45 000 (three runs) and those of molecular weight 280 000 (one run). The latter is more viscous and spreads more slowly, but they both follow eq 1. There is, however, one important difference. The high molecular weight polymer solution is wetting (see Figure 3). It shows peculiarities not seen elsewhere.

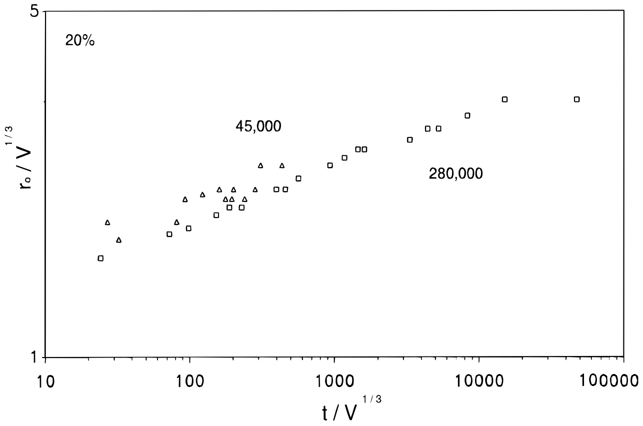

Figure 7. Comparison between 20% polystyrene of molecular weights 45 000 (three runs, from Figure 5) and 280 000 (one run) on glass. Both fluids are nonwetting.

As it spreads, a thin precursor film is formed ahead of the foot of the drop. This film had a thickness too thin to be seen by the goniometer, but it does exist because it changes the reflectivity of the glass. The junction of the bulk liquid and the precursor was seen to be unstable, showing a scalloped profile. As mentioned earlier, we saw unstable contact lines in our work below 5% polymer concentrations, and these have also been reported in the literature for poly(dimethylsiloxane).[22,23] However, they all occur at the very edge, unlike in the present case of a solution of high molecular weight polystyrene. Even though instabilities at the contact line have been known for some time, the reasons are not understood, except when the liquid contains one volatile compound and Marangoni instability sets in.[24] This cannot be the case for poly(dimethylsiloxane) mentioned earlier or for DBP used here because both DBP and PDMS are very nonvolatile (DBP boils at 350 °C). In addition, while dissolving, polystyrene DBP was heated and held at 90 °C, which would drive off most volatiles.

In Figure 7, we repeated the studies at 20% polymer concentration. Here, both systems are nonwetting with small equilibrium contact angles. They both show Zosel-type behavior, and the sharpness with which these systems equilibrate is seen vividly in the 280 000 molecular weight case.

As mentioned previously, we were prevented from studying the wetting kinetics for systems with higher polymer concentrations because of increasing equilibrium contact angles. Consequently, we looked for situations where the equilibrium contact angles would be smaller or zero (wetting). It was initially postulated that the nonzero contact angles were formed because of polymer adsorption. There are a few reasons against it, but it is obvious that adsorption can be eliminated or minimized if a low-energy surface, such as a PMMA surface, is used. PMMA has a critical surface tension of 39 mN/m and can be cleaned so that pure DBP wets it. Polystyrene (40%, MW 45 000) solution was used. It still showed an equilibrium contact angle of 7° versus 16° for glass. In Figure 8, the kinetic data for this system on glass and on PMMA are compared. As noted previously, the data on glass are Joos-type, but as seen here, the data on PMMA, where the equilibrium contact angle is much smaller, are Zosel-type.

It remains for us to discuss the possible effects of viscoelasticity on wetting kinetics. At low polymer concentrations, we observed no apparent effect, while at high polymer concentrations, the contact angles became large and spreading decreased. Consequently, we used a well-characterized viscoelastic fluid called Boger fluid.[25] It has a very high molecular weight polymer (10^6) at a very low concentration (0.1%). On glass, it gave an equilibrium contact angle of 10°, and the spreading was rapid and showed no anomalous behavior.

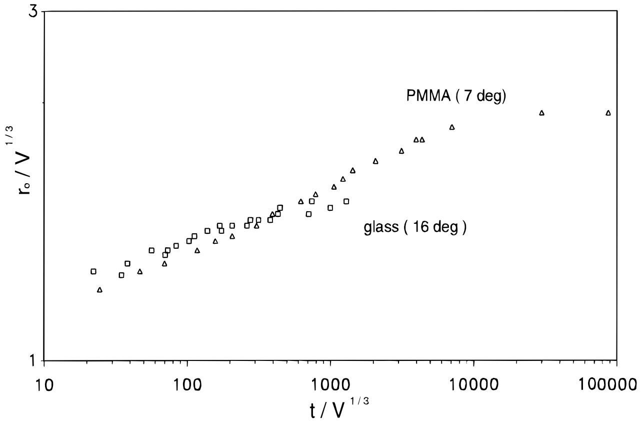

Figure 8. Comparison between 40% polystyrene of molecular weight 45 000 on glass (three runs, from Figure 5) and on PMMA (one run). Those on glass are Joos-type and those on PMMA are Zosel-type.

Discussion

One obvious conclusion from the present work is that almost all cases follow eq 1, even when the fluid is not Newtonian and not wetting! All profiles were those of segments of spheres. It is possible to suggest why the bulk of the profiles should show such a shape independent of the fluid rheology, and it is also possible to rationalize why shear thinning fluids will show the same response as Newtonian fluids, at least to a good approximation.

The pressure inside the drop, upon ignoring gravity because of the small drop sizes, is given by

$$p = -2M\gamma \tag{5}$$

where M is the mean curvature, and the atmospheric pressure has been set to 0. The drop makes an effort to reach equilibrium, which leads to a surface of constant curvature, that is, segment of sphere. However this is not compatible with the requirement that the contact angle at the contact line be at the equilibrium value (0 for wetting liquids). Consequently, a sharp change in curvature results near the contact line, which is visible under higher magnifications as in ellipsometry.[26] Thus, the driving force resides only in the vicinity of the contact line, and the drop shapes as seen under photomicrography are unaffected by rheology.

When the fluid mechanics at the contact line is to be considered, a slip velocity is needed for a complete analysis. We consider the slip velocity used by Neogi and Miller[8] to explain why eventually we do not see any special effects due to the non-Newtonian nature of the fluids. Their slip condition is in the form of Darcy's law:

$$v_r|_s = -\frac{k}{\mu}\frac{\partial p}{\partial r} \tag{6}$$

where k is the permeability. They showed that, to a good approximation, $3k \sim \sigma^2$, the variance of the roughness of the surface. The relevance of this slip condition lies in the fact that machine-polished metal surfaces have roughnesses in the 1−10 μm range. For glass it is 1−2 orders of magnitude lower. They obtained the wetting kinetics in terms of this parameter and fitted their results to one set of data to obtain a value for this parameter. The value obtained compared well with the value measured by Talysurf.

One can extend the procedure to non-Newtonian fluids. As most of those of interest are shear thinning, we use Ellis' model:

$$\mu_o/\mu = 1 + (\tau_{zr}/\tau_{1/2})^{\alpha-1} \tag{7}$$

where α is greater than 1. When the drop has spread sufficiently to appear flat and thin, the lubrication theory approximation applies. The details of the derivation leading to the average velocity in the tangential direction

$$\langle v_r\rangle = \frac{Z}{3\mu_o}(h^2 + 3k) - \frac{(-hZ)^{\alpha}}{h\mu_o\tau_{1/2}^{\alpha-1}}\left(\frac{h^2}{\alpha + 2} + k\right) \tag{8}$$

where $Z = -\partial p/\partial r = \gamma(\partial/\partial r)[\partial^2 h/\partial r^2 + (1/r)(\partial h/\partial r)]$ is the driving force, are given in the Appendix. It is known from previous work that $\mathrm{d}r_o/\mathrm{d}t$, the rate of spreading, equals $v_r|_{z=0}|_{r=r_o}$, the slip velocity at the contact line, which equals $\langle v_r\rangle|_{r=r_o}$, the average velocity at the contact line.

Consequently, if in eq 8 we take the limit as the contact line is approached, drop thickness h goes to 0, radial position r goes to r_o, and the driving force Z reaches a finite nonzero value in the presence of slip. It is easy to see that, in that limit, the first term on the right-hand side representing the Newtonian part reaches a finite and nonzero limit. But the second term on the right-hand side in eq 8 representing the shear thinning effect becomes 0. Thus, the non-Newtonian part has no effect there. As discussed earlier, $Z = 0$ in the interior, and the non-Newtonian part is also of no consequence there. In effect, for a shear thinning fluid, the non-Newtonian part does not play a role, a result also obtained by Voinov[27] using different scaling arguments.

It is much more of a problem to determine, if viscoelasticity has no effect on the dynamics, where the latter is expected to appear as a near-discontinuity in the response. There does not appear to be any discontinuities in drop shapes, which are uniformly that of spherical caps. However, the Zosel-type spreading rates *are* discontinuous. Whether or not they arise out of viscoelasticity will need to be determined. (The Zosel-type rates seen here and in Zosel's[15] work appear only when the fluid is a polymer solution.) The fluid mechanical calculations shown for a non-Newtonian fluid cannot be used this easily for a viscoelastic liquid, and an attempt to obtain a numerical solution will be considered at a later date.

We have used eq 1 to correlate our data, which in a different form is known as Tanner's law.[5] Differentiation of eq 1 leads to the result that $\mathrm{d}r_o/\mathrm{d}t \propto r_o^{-9}$. For small values of θ, eq 4 becomes $\theta \simeq 4V/(\pi r_o^3)$. By combining the two, we have $\theta^3 \propto \mathrm{d}r_o/\mathrm{d}t$, which with the proper coefficients is Tanner's law for *wetting liquids*. It is important to emphasize that, whereas our data satisfy all correlations for a wetting liquid, our liquids are actually nonwetting, and these correlations are not capable of showing equilibration at large times, much less the very sharp turn to equilibrium that our data show.

The extensions of Tanner's law to nonwetting liquids take various forms:

$$\theta^3 - \lambda^3 = 9Ca^{\mathrm{o}} \tag{9a}$$

$$(\theta^2 - \lambda^2)\theta = Ca^{\mathrm{o}} \tag{9b}$$

where θ is the apparent dynamic contact angle, λ is the equilibrium contact angle, and Ca^{o} is the capillary number based on the wetting rate. Now $\theta > \lambda$, and they are equal at equilibrium. As the power on λ is high, λ^2 and λ^3 on the left-hand side are negligible when λ is small. The dynamics is unaffected by this term until θ gets to be *very* close to λ. This suggests that one may have an almost discontinuous behavior in this case. A numerical plot showed that the actual response was quite different, in that only the cases of *large* equilibrium contact angles were marked by abrupt changes, and thus eqs 9a and 9b are inadequate in explaining sudden equilibration. Other rate expressions for nonwetting liquids, such as the one by Neogi and Miller,[8] show only Joos-type continuous equilibration.

The suggestions that Zosel-type behavior is due to a variety of continuum effects ignore the molecular phenomena near the contact line. Undoubtedly, these are important and could explain why a fluid of low surface energy cannot wet a high-surface-energy solid. Since a low-energy substrate decreases the contact angle but does not make the solution wetting, one assumes that polymer adsorption is at least not the leading contributor. The adsorption of polymer itself appears to be independent of molecular weight,[28] and yet the present phenomenon is quite sensitive to molecular weight. It is possible instead that steric exclusion of polymers from the corner near the contact line may be important. Cazabat[7] has shown that packing constraints in thin films near the contact line can be used to understand the fine structure of wetting under both static and dynamic conditions. Such methods were used earlier by Frumkin[29] and Deryaguin[30] in nonpolymeric systems. The subject of disjoining pressure in thin films of polymer solutions is a very large one[31] and will be considered separately. It is sufficient to state here that it has been shown that the disjoining pressure in a thin film can increase with decreasing film thickness. Obviously such films do not like to thin and, hence, may very well be nonwetting. One other suggestion of why polymer solutions behave oddly at the dynamic contact line has been that the polymer molecules change conformation there.[32]

A list is included to help one focus on our main results and conclusions: (i) One of our major findings is that of a lack of wetting by polymer solutions. It is probable that it is caused by the problems encountered in packing polymer molecules in thin films. We were unable to find any other explanation based on *equilibrium* phenomena. (ii) Experimentally, one goes from the Zosel type of spreading to the Joos type with increasing polymer concentration and increasing contact angles. It is the actual values of the contact angles that have the strongest influence. (iii) It is Zosel-type behavior that is unusual, and our work validates the one set of data reported by Zosel over a wider range of conditions and changes in the key variables. These spreading data follow eq 1 and Tanner's law for wetting fluids, even though the fluids used here are nonwetting. The spreading halts suddenly, which is also very surprising. (iv) These peculiar dynamics could be caused by the aforementioned thin film phenomenon or in the other extreme because of the viscoelastic nature of the polymer solution. At present these mechanisms are under study. (v) Unstable contact lines are seen for fast-spreading drops (below 5% polystyrene), where the instability is probably caused by inertial effects. Only in one case of wetting liquid among the polymer solutions shown in Figure 3 is an instability seen in the vicinity of the contact line under slow spreading conditions. Whereas the Marangoni effect is not expected, those arising from thin film phenomena[33] and viscous fingering are well-known[34] and could give rise to the scalloped profiles in this case. (vi) Non-Newtonian (nonlinear) rheological properties and adsorption do not appear to be significant.

Acknowledgment. We thank Dr. Kurt Koelling, Department of Chemical Engineering, Ohio State University, for supplying us with a sample of Boger fluid.

Appendix

Under lubrication theory approximation, the equations of motion become

$$0 \simeq -\frac{\partial p}{\partial z} \tag{A1}$$

$$0 \simeq -\frac{\partial p}{\partial r} - \frac{\partial \tau_{zr}}{\partial z} \tag{A2}$$

The normal stresses become negligible if the drop is flat and thin. By integrating eq A2 once subject to the boundary condition $\tau_{zr} = 0$ at $z = h$, one obtains

$$\tau_{zr} = -\frac{\partial p}{\partial r}(z - h) = Z(z - h) \tag{A3}$$

where it is evident from eq A1 that the driving force, $-\partial p/\partial r = Z$, is independent of z.

Equation 7 is inverted to

$$\frac{\mu}{\mu_o} = \frac{1}{1 + [\tau_{zr}/\tau_{1/2}]^{\alpha-1}} \tag{A4}$$

and by multiplying both sides by $-\mathrm{d}v_r/\mathrm{d}z$, we get

$$\frac{\tau_{zr}}{\mu_o} = \frac{-(\mathrm{d}v_r/\mathrm{d}z)}{1 + [\tau_{z\gamma}/\tau_{1/2}]^{\alpha-1}} \tag{A5}$$

This rearranges to

$$\frac{-\mathrm{d}v_r}{\mathrm{d}z} = \frac{Z}{\mu_o}(z - h) + \frac{Z^\alpha}{\mu_o \tau_{1/2}^{\alpha-1}}(z - h)^\alpha \tag{A6}$$

upon use of eq A. Integration leads to

$$-v_r = \frac{Z}{2\mu_o}(z - h)^2 + \left(\frac{z^\alpha}{\mu_o \tau_{1/2}^{\alpha-1}}\right)\left(\frac{(z - h)^{\alpha+1}}{\alpha + 1}\right) + C_1 \tag{A7}$$

By substituting eq 7 into the slip boundary condition, eq 6, and then using eq A3, we get

$$v_r|_{z=0} = \frac{k}{\mu_o}\left[Z + \frac{Z^\alpha(-h)^{\alpha-1}}{\tau_{1/2}^{\alpha-1}}\right] \tag{A8}$$

By using eq A8, we can eliminate the constant of integration, C_1, in eq A7. By integrating v_r over the drop thickness and dividing by it, we obtain the averaged tangential velocity:

$$\langle v_r \rangle = \frac{Z}{3\mu_o}(h^2 + 3k) - \frac{(-hZ)^2}{h\mu_o \tau_{1/2}^{\alpha-1}}\left(\frac{h^2}{\alpha + 2} + k\right) \tag{A9}$$

which appears as eq 8 in the text.

References and Notes

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