Dynamic Contact Angles of Shear Thinning Fluids

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Introduction

The data on spontaneous spreading kinetics of shear thinning liquids show no effects of the non-Newtonian rheology. This has also been demonstrated using a theory which shows that the viscosity to be used for correlation is the zero shear viscosity. However, recent data on forced spreading show deviations. It has been shown here that if the correct correlation is chosen, then the aforementioned data do conform to that for a Newtonian fluid as expected.

The first experiments on wetting kinetics appear to be conducted by Schonhorn et al.[1] for spontaneous spreading of small drops of polymer melts on glass and metals. The interesting observation to make there (and one that was not made by the investigators) is that no effect of non-Newtonian behavior of polymer melts could be observed. A nominal viscosity of each was all that was needed to obtain a general correlation.

Later, Nieh et al[2] also found the same behavior in polymer solutions. A closer look at an earlier model (Neogi and Miller[3]) for Newtonian liquids indicated that the shear thinning behavior should not be observed, and the correct viscosity to use would be the zero shear viscosity. Neogi and Ybarra[4] found the same result by using a method for calculating dynamic contact angle (α) as a function of capillary number ($Ca = \mu U/\gamma$, where μ is the viscosity, U is the contact line velocity, and γ is the surface tension) given by de Gennes.[5] The method equates viscous dissipation in a wedge to the surface work done and has been given a brief fluid mechanical justification by Neogi.[6] Neogi and Ybarra[4] also observed that neither viscoelasticity nor normal stresses could affect spontaneous spreading. These findings were later verified by Barone,[7] Rafai et al,[8] Boudaoud[9] and Scarpulla et al.[10]

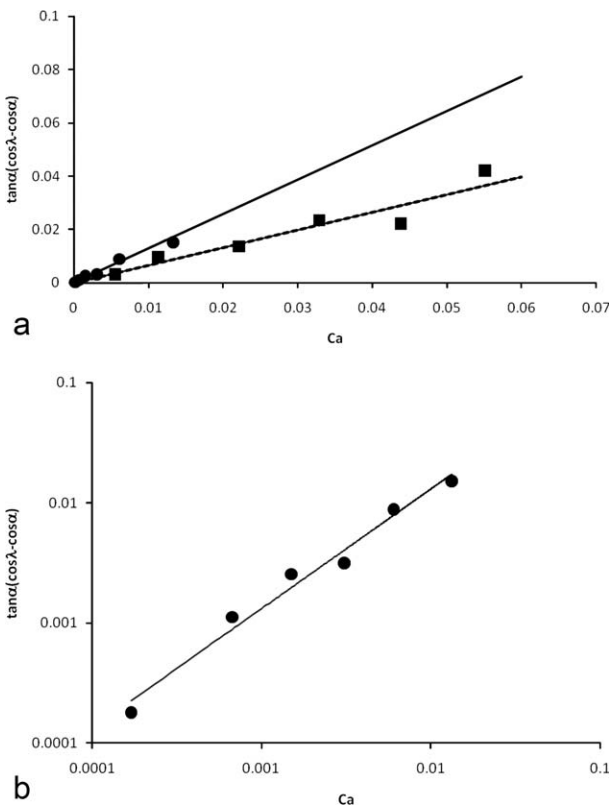

Figure 1. (a) Plots of data from Seevaratnam et al[11,14] for xanthan gum following Eq. 1. (b) The low points for 0.15% xanthan gum from Figure 1a have been shown in an expanded plot.

The black circles are for 0.15% and the bold line is about 1.29.Ca and the equilibrium contact angle $\lambda = 13.9°$. The gray squares are for 0.25% and the dashed line is 0.65.Ca. Here, $\lambda = 21.8°$.

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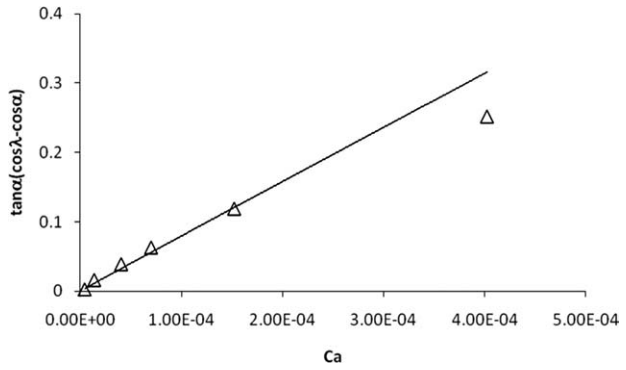

Figure 2. Plot of 1% cmc from Wang et al[12] and Lee[16] shown following Eq. 1.

The fitted line is 734.45.Ca, fitted with $\lambda = 25.4°$ whereas measured $\lambda = 20.2°$.

However, more recently Seevaratnam et al[11] and Wang et al[12] have produced data using forced spreading which do not conform to the Newtonian behavior contrary to the expectation raised from the behavior observed on spontaneous spreading. These researchers used their own theories and not de Gennes' to evaluate the above. Thus, if it is continued to be assumed that shear thinning liquids behave as Newtonian fluids during wetting, de Gennes' result[13] becomes

$$\tan\alpha(\cos\lambda - \cos\alpha) = Ca \ln|1/\varepsilon|.3 \qquad (1)$$

where λ is the equilibrium contact angle and ε is the dimensionless cutoff thickness used to exclude the very small region contacting the contact line. In Eq. 1 simplifications for small angles in the trigonometric functions have not been carried out, although small values of α and λ have been assumed in the derivation.

Figure 1a shows that data of Seevaratnam et al[10,14] for xanthan gum (mol. wt. 2×10^6) replotted using Eq. 1. The black circles are the data of 0.15% polymer. The data were fitted to an algebraic expression of $y = a.x^b$ for varying equilibrium contact angle λ, until b became approximately 1.0. The resulting line of $y = 1.2891.x^{0.9967}$, has been plotted in bold. The resulting equilibrium contact angle $\lambda = 13.9°$ compared to 6.3° obtained by the researchers. The data for the 0.25% solution are shown in black squares. For this case, $\lambda = 21.8°$ against the reported value of 8.5° in the experiments, the line is given by $y = 0.6521.x^{0.9952}$ and has been shown as the dashed line. Since the data for 0.15% xanthan gum is very compressed in Figure 1a, they have been shown in an expanded form in Figure 1b. One feature of polymer solutions is that they tend to be nonwetting as a rule even when the pure solvent is wetting.[2,15] This happens due to the fact that the region of the contact line is inhomogeneous in the polymer chain segment density that changes with polymer concentration and molecular weight. This change has been used to explain the differences in the equilibrium contact angles and may also be used to explain the differences in the cutoff length which leads to differences in slopes in Figure 1.

The data of Wang et al[12] (communicated by Lee[16]) could be fitted to Eq. 1 when the first data point at $Ca = 1.52 \times 10^{-4}$ was ignored. This is shown for 1% carbomethylcellulose (cmc) sulfate solution (mol.wt.700, 000) in Figure 2. The measured equilibrium contact angle was $\lambda = 20.2°$, but the one used for fitting to Eq. 1 is $\lambda = 25.4°$ The fitted line shown in bold is $y = 734.45.x^{0.9915}$. It should be noted that the data of Wang et al[12] for α have been obtained through a force balance where the forces taken to move a plate in or out were measured. On the other hand, the values of α by Seevaratnam et al[10] were obtained by measuring the profile. One key feature in measuring small equilibrium contact angles from photography or images is that the accuracy drops for values below 10° and around 5° is not trustworthy, although better than qualitative judgments can be made.[17] Generally, the angles in this region are measured using interferometry.[18] The equilibrium contact angles reported by Seevaratnam et al[11] fall below 10° and its accuracy may be questioned, but present estimates are uncomfortably far from the reported values. In case of Wang et al[12] the difference between the reported value and the value calculated here is not significant.

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