Measurements of the viscosity of thin fluid films between two surfaces with and without adsorbed polymers

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Abstract: A new method has recently been introduced for making detailed measurements of hydrodynamic effects in very thin liquid films between two surfaces. The method is used to obtain viscosity profiles, i. e. the viscosity as a function of the separation, between surfaces with adsorbed polymer layers. Results are presented for pure cyclohexane between two mica surfaces and for polystyrene ($M_w = 9 \times 10^5$) adsorbed onto mica from cyclohexane at 26 °C (i. e. below the θ-temperature of 34.5 °C). The range of distances over which the concept of an effective "hydrodynamic layer" is applicable is established, and a simple correspondence is found between the effective hydrodynamic thickness, the radius of gyration of the polymer and the range of the steric force between the two polymer-covered surfaces. Further experimental evidence is presented which suggests that, depending on the solvent conditions, similar correlations apply more generally to other polymer systems.

Key words: Hydrodynamic thickness, polymer adsorption, thin film viscosity, steric interactions, surface rheology.

Introduction

It has long been suspected that a surface may modify the viscosity η of a liquid adjacent to it. Any such effect is likely to occur by a gradual change in η close to the surface, but it is usually modelled in terms of an immobilized solvent layer of thickness Δ at the interface, equivalent to shifting the "shear plane" from the interface (at $D = 0$) to $D = \Delta$. Similar concepts apply to polymer covered surfaces, where Δ is commonly referred to as the "hydrodynamic thickness" of the (usually adsorbed) polymer layer.

The understanding of such effects is important for interpreting the viscosities of colloidal dispersions and the flow rates of liquids through porous media and capillaries, for calculating the rotational and translational diffusion of small particles (e. g. micelles), and for obtaining zeta potentials from electrophoretic measurements.

Additional perturbations may arise when a liquid is confined between *two* surfaces close together, for example, within a thin surface film or in the small space between colloidal particles. Here, any modification of

the liquid viscosity will influence such phenomena as the drainage of thin films, the viscous forces associated with (hydrodynamic) interparticle interactions and coagulation rates, and in lubrication and rheological processes.

Concerning the positions of shear planes of *pure* liquids near surfaces, the results of a number of indirect measurements [1–4] of the viscosities of aqueous solutions at surfactant-water interfaces (such as occur in micelles and soap films) place the shear plane within a few Ångströms of the head-groups (i. e. $\Delta \approx 0$), whereas for solid-liquid interfaces Δ values in the range 10–50 Å (and sometimes well in excess of 100 Å) have been reported [1, 5–9].

Recently a new experimental technique has been introduced [10], which uses a Surface Forces Apparatus [11], and which can directly measure the viscosity $\eta(D)$ of any liquid in the region between two molecularly smooth surfaces as a function of the separation distance D between them. Results were given only for pure liquids [10]. These showed that the viscosities of tetradecane and water between two curved mica sur-

faces are within about 10 % of their bulk values in films as thin as 50 Å or less, and that the shear plane is within a few Ångströms of each solid-liquid interface (i. e., that *at most* one layer of liquid molecules is immobilized at each surface). These conclusions were not changed in the presence of electric double-layer overlap forces or solvation (i. e., structural or hydration) forces, and it was further concluded that solvent structuring at surfaces does not necessarily affect the liquid viscosity.

Chan and Horn [12] have also recently used a Surface Forces Apparatus but employed a different dynamic technique to measure the rate at which a thin film of liquid drains from between two curved mica surfaces as they are forced together. For the three non-polar liquids studied they obtained excellent agreement with the "Reynolds theory" of lubrication but only when the shear plane was placed at 1–2 molecular diameters (layers) from the mica surface.

The apparent success of these new dynamic techniques appears to open up new possibilities for very detailed studies of a variety of hydrodynamic, viscoelastic, hysteretic and other time-dependent phenomena in complex solvent systems, and in particular to surfaces with adsorbed polymers where there is already a voluminous literature on the subject (reviewed in [13]). The hydrodynamic thicknesses A_H of adsorbed polymer layers have previously been measured using capillary viscometers [14,15] and sintered glass disc viscometers [16], and more recently by quasielastic light scattering [17] and photon correlation spectroscopy [18]. The results on a variety of different polymer-solvent-surface systems have shown that above saturation adsorption A_H values are typically between one and two radii of gyration — the higher values being obtained for better than Θ conditions (good solvents). We return to consider these results again in the Discussion.

Here I chose to study the previously well-characterized system of polystyrene adsorbing onto mica surfaces from cyclohexane [19–21]. The aims were (i) to measure the effect of polymer adsorption on the viscosity profile $\eta(D)$ of the fluid film (which includes solvent, adsorbed polymer and some free polymer) between the two surfaces, (ii) to establish the distance beyond which the concept of an effective hydrodynamic thickness A_H is valid or useful, (iii) to investigate the effect of shear rate on A_H, and (iv) if possible, to relate these viscous effects to the "steric interaction" force-law between the two polymer-covered surfaces. Finally, some preliminary measurements were also

made on two completely different polymer systems to test whether the results and conclusions obtained from the PS-cyclohexane system may be expected to apply more generally.

Experimental

Viscosity measuring technique

A fairly detailed description of the experimental method has been given before [10–12] and only a very brief account will be given here. The Surface Forces Apparatus itself consists of a liquid-filled steel chamber within which two curved mica sheets, glued onto quartz-glass discs, are mounted with their surfaces facing each other. The upper surface is attached to a piezoelectric crystal while the lower is supported at the end of a weak double-cantilever spring, also referred to as the "force-measuring spring". The distance D between the two surfaces can be controlled to better than 1 Å, and independently measured to the same accuracy by an optical interference technique using Fringes of Equal Chromatic Order (FECO).

The method employed for measuring the fluid viscosity involves applying an a. c. voltage to the piezoelectric crystal which causes the upper surface to oscillate (with amplitude A_o and frequency ν). The hydrodynamic (or viscous) force between the two surfaces causes the lower one to oscillate at the same frequency but at a different amplitude B_o and phase Θ. What can be easily measured, however, is the amplitude of vibration A of the separation between the two surfaces, viz. $A = |A_o - B_o e^{i\Theta}|$. At large surface separations D the lower surface will hardly move during the oscillations of the upper because the viscous coupling is weak, i. e., $B_o \ll A_o$ and so $A \approx A_o$ for large D. At small surface separations the viscous coupling is strong and the two surfaces move in concert, i. e. $A \rightarrow O$ as $D \rightarrow O$. In the absence of any intermolecular force between the two surfaces (i. e. when the only opposition to flow is due to fluid viscosity), it may be shown [10] that at any mean distance D the viscosity of the film $\eta(D)$ is given by

$$\eta(D) = \frac{KD}{12\pi^2 R^2 \nu} \left[\left(\frac{A_o}{A} \right)^2 - 1 \right]^{1/2} \quad \text{(for } A \ll D) \quad (1)$$

where K is the stiffness of the supporting spring and R the effective hydrodynamic radius of the curved surfaces (defined by $R \approx \sqrt{R_1 R_2}$ where R_1, R_2 are the respective radii of the two cylindrical mica surfaces). Equation (1) assumes no slip at $D = O$.

Experimentally, the amplitudes A were measured (to ± 1 Å) by connecting a video camera (DAGE MTI, model 65) and recorder (Sony) to the exit of the spectrometer, and recording the moving FECO fringes during the cycling of the surfaces, as described in [10] and [12].

Experimental procedure

The forces $F(D)$ were first measured in pure dry cyclohexane (Fluka, spectroscopic grade) as previously described [22]. This was followed by a "viscosity run" whereby the camera was used to record the decreasing amplitudes A as the two oscillating surfaces were slowly brought towards each other. A concentrated Polysty-

rene (PS)-in-cyclohexane solution was then injected into the chamber and the contents thoroughly stirred to give a final PS concentration of 12×10^{-6} g/ml. The two surfaces were then separated by ~ 2 mm and the PS was then allowed to adsorb onto them until, after about 16 h, saturation (equilibrium) adsorption was attained [19–21]. The polystyrene was a 900,000 mol. wt. monodisperse standard from Pressure Chemical Co. (further purified as described in [21] and kindly supplied by Matt Tirrell). The unperturbed radius of gyration of this PS in cyclohexane is approximately $R_g \simeq 260$ Å [23], and the Θ-temperature is 35 °C.

After equilibrium was attained the forces and viscosity were again measured (in the same way as before addition of PS). All measurements, including the force runs, polymer adsorption and viscosity runs, were done at the same temperature of 26 °C (to avoid any possible clouding of the polymer solution) in a constant temperature room.

Results

Polystyrene in cyclohexane

Figure 1 shows results for pure cyclohexane and for PS in cyclohexane at full surface coverage. Rather than plot $\eta(D)$ against D, as given by Equation (1), it is more instructive to plot $12\pi^2 R^2 v / K [(A_o/A)^2 - 1]^{1/2}$ against D (as has been done in the figure), since the inverse slope of the plotted "line" gives the viscosity and the intercept of the line with the distance-axis gives the shear

plane [10]. Further, by noting the way the results, so plotted, deviate from a straight line passing through the origin, one can immediately recognize the difference between a gradual change in viscosity from a simple shift in the position of the shear plane.

Figure 1 shows that in pure cyclohexane the viscosity of the liquid is the same as in bulk with no apparent deviation down to the smallest distances. The line passes through the distance-axis at $D = 2\Delta = -4 \pm 10$ Å, i. e. $\Delta = -2 \pm 5$ Å *per surface*. We conclude therefore that within experimental error the shear plane is at $D = 0$ (the mica-liquid interface), and — as previously found for pure tetradecane and water [10] — the results confirm that *at most* one layer of liquid molecules is immobilized at each surface (note: the molecular diameter of cyclohexane is about 6 Å). The force-law measured in the pure cyclohexane is not shown, but was the same as previously reported [22], viz. a decaying oscillatory force (structural solvation force) extending out to about 30 Å, beyond which it merges with the weak monotonically attractive van der Waals force.

The second curve and inset in Figure 1 show the results obtained for the viscosity and force-law in the PS solution. It is immediately apparent that the major
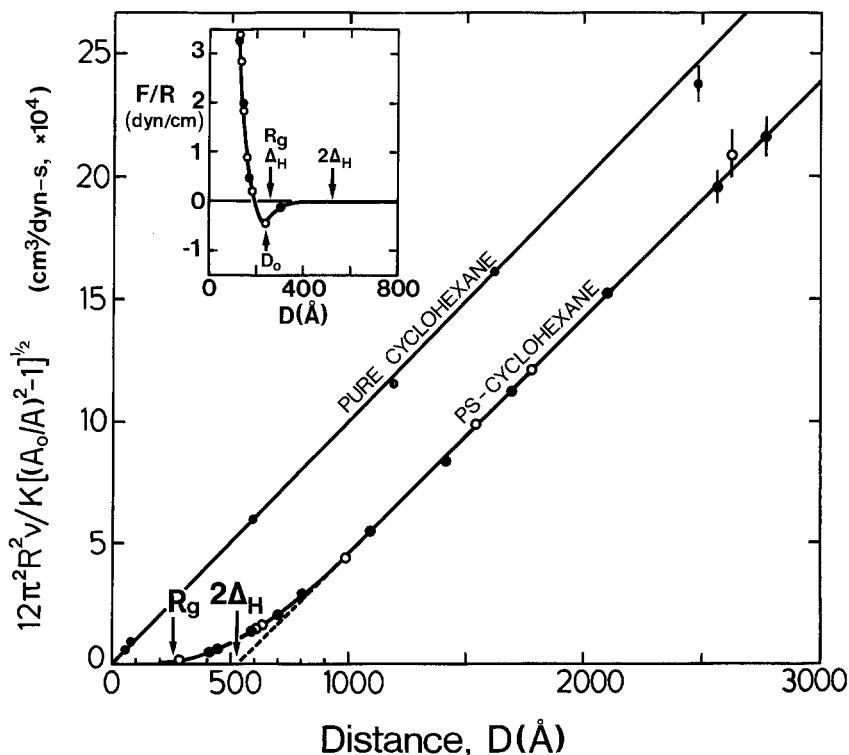

Fig. 1. Plot of $12\pi^2 R^2 v / K [(A_o/A)^2 - 1]^{1/2}$ against distance D in cyclohexane and in a PS-cyclohexane solution after the PS ($M_w \simeq 900,000$, $R_g \simeq 260$ Å, $T_\Theta \simeq 35$ °C) had adsorbed on the mica surfaces (all measured at 26 °C). Ideally, if the viscosity equals the bulk value at all distances the points would fall on a straight line passing through the origin whose inverse slope gives the viscosity. In pure cyclohexane this is the case. For the polymer covered surfaces the line is shifted outwards by about 520 Å, corresponding to an effective hydrodynamic layer of thickness $\Delta_H \simeq 260$ Å per surface. Identical results were obtained at two driving frequencies of $v = 1$ Hz (closed circles) and $v = 0.15$ Hz (open circles). The inset shows the reversible force-law (Force/Radius versus D) measured in the PS-cyclohexane solution just before the viscosity run: on compression (closed circles), on decompression (open circles).

effect of polymer adsorption is to shift the hydrody-namic (shear) plane from $D = 0$ to $D = \Delta_H \approx 260\,\text{Å}$ *per surface*, which we may note is the same as the value of R_g for this PS. From the slope of the curve we may further note that at separations D beyond about 3 R_g from contact (about R_g from the hydrodynamic planes) the viscosity of the film is already varying in the same way as if it were bulk solution (N. B. the bulk viscosity of the dilute 12×10^{-6} g/ml PS-cyclohexane solution is practically the same as that of pure cyclohexane).

The region between $D \simeq 3\,R_g$ down to $D \simeq R_g$ may be identified as some sort of transition region where the effective viscosity deviates markedly from its simple long-distance linear behaviour (by $D < R_g$ it has risen to more than 20 times the bulk value and becomes difficult to measure). Indeed, in this short-distance regime (where complex polymer overlap re-laxation processes are occurring) it is not clear whether the concept of a simple Newtonian viscosity remains valid. Since any such relaxation effects would be expected to depend on the shear rate it was decided to record the viscosity at two different frequencies, viz. at ~ 1 Hz and ~ 0.15 Hz. The results of these two runs were identical (Fig. 1), even in the critical transition region at surface separations below 3 R_g.

The inset in Figure 1 gives the reversible force-law measured in the PS-cyclohexane system. The results are very similar to those previously reported for this system at the same solution concentration and tempe-rature [21], and exhibit the expected strong steric repulsion at separations below ~ R_g with a weakly attractive regime at larger distances, characteristic of polymer interactions below the θ-temperature in nonaqueous solvents [19, 20, 24]. Note that the repul-sive steric force has a shorter range than the smallest distance at which the viscosity was measured. By using a stiffer spring it would have been possible to measure η at even smaller distances, where the surfaces interact, and then analysing the results using a modified form of Equation (1) (see Ref. [10], Eq. (A12)). However, given the possibility that complex rate-dependent hysteresis and other relaxation effects may be occuring in this strong overlap regime, it was decided to defer this more difficult experiment to some future date.

Other polymer systems

Two other polymer systems were studied: a *polymer melt* and a *crude oil* system. The results pertaining to the thin film viscosity of these systems will be briefly

described here; detailed accounts of these experiments (and the nature of the force-laws) will be published elsewhere in co-authorship with Roger Horn and Hugo Christenson.

The polymer melt system was a pure poly-dime-thylsiloxane liquid of mean $M_w \approx 3,700$ (i. e. 50 seg-ments) and with a bulk viscosity of about 50 cP at 22 °C (the temperature at which these measurements were made). The polysiloxane was obtained from Dow Chemicals and used without further purification. The physical properties of open chain dimethylsiloxa-nes have been described by Hunter et al. [25].

If one considers that the radius of gyration of the polysiloxane is about 16 Å [23] the force and viscosity results were qualitatively similar to, though of longer range than, those obtained with PS adsorbing from cyclohexane solution: There was a strong steric repul-sion at distances below 30 Å, and the fluid exhibited bulk viscosity beyond a surface separation of about 55 Å, corresponding to $\Delta_H \approx 27\,\text{Å}$ per surface. Both these distances are now closer to *twice* the value of R_g for this polysiloxane (though this may also be partly due to the likely polydispersity of this commercial polymer).

The crude oil system consisted of two samples obtained from two Australian reservoirs from Barrow Island. The oil from this region is considered to be light, of viscosity around 5 cP. The results (obtained at 22 °C) showed that the forces between mica surfaces immersed in these oils are dominated by adsorption of medium to high molecular weight components which are known to be present in small amounts in all crude oils [26]. Thus, the results were now qualitatively very similar to those measured in the PS-cyclohexane system; viz. a weak long-range attractive force turning into a steeply repulsive steric force at smaller separa-tions. Both the repulsive wall and the position of the force minimum moved out slowly with time (e. g., from ~ 25 Å to ~ 60 Å over a 24 h period in one sample studied), indicative of further adsorption or replacement of low mol. wt. components by high mol. wt. components. At the same time the viscous proper-ties of the fluid in the gap could again be described by assigning an effective hydrodynamic plane, which also moved out with time in proportion to the increasing range of the steric force. Thus, for the sample mention-ed above, as the force minimum moved out from $D_o = 25\,\text{Å}$ to $D_o = 60\,\text{Å}$, the hydrodynamic plane had moved from $\Delta_H = 20\,\text{Å}$ to $\Delta_H = 50\,\text{Å}$. On comparing these values with the positions of the minimum and slipping plane in the PS-cyclohexane system (where

$D_o \approx \Delta_H \approx 260$ Å, see Fig. 1), it is striking to find that $D_o \approx \Delta_H$ in all three cases.

Discussion and conclusions

The results of these and previous experiments show that while the structuring of pure liquids at surfaces has no significant effect on the hydrodynamic flow beyond the first layer of molecules, the effect of an adsorbed polymer layer is quite dramatic, with the hydrodynamic plane (shear plane) being shifted far out into the solution where the density of segments (trains, loops and tails) is extremely low and where the tails effectively determine the flow behaviour [13,17, 18,27].

The results show that for PS adsorbed on mica in worse than θ-conditions the concept of an *apparently immobilized* „hydrodynamic layer" of thickness Δ_H per surface is valid at distances greater than 1.5-2.0 Δ_H from each surface, while the value of Δ_H itself is very close to the unperturbed radius of gyration, viz. $\Delta_H \simeq R_g$. This contrasts with a number of significantly higher values previously reported for Δ_H, in the range $(1.5-2.0) R_g$, based on viscometric and light-scattering experiments [13–18] as well as various theoretical analyses [18,27] which predict $\Delta_H \alpha \sqrt{M_w}$ in general, and $\Delta_H \simeq 2 R_g$ for high molecular weight polymers $(M_w \sim 10^6)$. However, these experimental and theoretical studies were all involved with polymers adsorbed from θ-solvents or from good solvents, where the values for R_g are expected to be higher than in worse than θ-conditions, and where the adsorbed segments are expected to extend over a longer range [13,17,28,29]. This is consistent with our preliminary results for the ~ 3700 mol. wt. polydimethylsiloxane melt system, where for this θ-solvent $\Delta_H \simeq 1.7 R_g$; and we may also note reports of increased adsorbed layer thicknesses with increasing temperature in a number of different polymer systems in nonaqueous solvents [28,29].

We may therefore tentatively conclude that the results of quite a number of different experiments (including those reported here) all indicate that at full surface coverage the hydrodynamic thickness increases as one passes from poor to good solvent conditions (from about $\Delta_H \simeq R_g$ to $\Delta_H \simeq 2 R_g$, where R_g is the unperturbed radius of gyration), though more systematic experiments are needed to establish the validity and generality of this conclusion.

Similar correlations emerge when we compare the viscosity results with the steric interactions in the three polymer systems studied. For the PS-cyclohexane system the range of the steric repulsion, defined — somewhat arbitrarily — by the position of the minimum in the force-law, was almost exactly the same as the hydrodynamic thickness, viz. $\Delta_H \simeq R_g \simeq D_o$ (see Fig. 1 inset). For the less well-defined crude-oil system (of unknown R_g) there was a similar correlation, where now $\Delta_H \simeq 0.8 D_o$. Klein and coworkers [20, 24] have already pointed out that there is a direct 1:1 correspondence between the range of the repulsive forces (or D_o) and R_g (or $\sqrt{M_w}$) in PS-cyclohexane systems in worse than θ-conditions. Interestingly, on transferring PS to the good solvent cyclopentane the range of the repulsion approximately doubles, going from $D \simeq R_g$ to $D \simeq 1.7 R_g$ [24], with the concomitant disappearance of the attractive tail [24, 30]. Similarly, for the θ-solvent polysiloxane melt system (where $R_g \simeq 16$ Å and $\Delta_H \simeq 1.7 R_g$) the steric repulsion was at $D \simeq 30$ Å, i.e. close to 2 R_g.

These results are again consistent with the earlier conclusion, and lead to the second tentative conclusion of this paper that there is also a direct correlation between the position of the hydrodynamic plane and the range of the repulsive steric interaction.

More systematic experiments are needed, especially at different temperatures, a wider range of shear rates, and penetrating deeper into the overlapping region ($D < R_g$) to obtain a full understanding of the flow of fluid and segmental relaxation processes at polymer-covered surfaces. On the theoretical side, while the results are in accord with modern theories of the effective hydrodynamic thickness of adsorbed polymers a more detailed comparison must await theories which give the actual viscosity profile between two surfaces.

References

1. Hunter RJ (1981) Zeta Potential in Colloid Science, Academic Press, New York London, Ch 5
2. Mysels KJ, Cox MC (1962) J Coll Interf Sci 17:136
3. Lyklema J, Scholten PC, Mysels KJ (1965) J Phys Chem 69:116
4. Carrol BJ, Haydon DA (1975) J Chem Soc Faraday Trans I 71:361
5. Strenge Von K (1978) Z Phys Chem (Leipzig) 259:102
6. Derjaguin BV (1976) Chem Scripta 9:97
7. Churaev NV, Novikova AV, Petrov AK, Zorin ZM (1974) J Coll Interf Sci 48:374

8. Drost-Hansen W (1982) In: Franks F, Mathias S (eds) Biophysics of Water Wiley, New York, p 163
9. Hough DB, Ottewill RH (1983) Progr Coll & Polym Sci 68:101
10. Israelachvili JN (1986) J Coll Interf Sci 110:263
11. Israelachvili JN, Adams GE (1978) J Chem Soc Faraday Trans I 74:975
12. Chan DYC, Horn RG (1985) J Chem Phys 83:5311
13. Takahashi A, Kawaguchi M (1982) Adv Polym Sci 46:1
14. Öhrn OE (1958) Ark Kemi 12:397
15. Priel Z, Silberberg A (1978) J Polym Sci 16:1917
16. Rowland FW, Eirich FR (1966) J Polym Sci 4:2033, 4:2401
17. Kato T, Nakamura K, Kawaguchi M, Takahashi A (1981) Polym J 13:1037
18. Cohen Stuart MA, Waajen FHWH, Cosgrove T, Vincent B, Crowley TL (1984) Macromolecules 17:1825
19. Klein J (1980) Nature 288:248; (1982) Adv Coll Interf Sci 16:101
20. Klein J (1983) J Chem Soc Faraday Trans I 79:99
21. Israelachvili JN, Tirrell M, Klein J, Amog Y (1984) Macromolecules 17:204
22. Christenson HK, Horn RG, Israelachvili JN (1982) J Coll Interf Sci 88:79
23. Brandrup J, Immergut EH (1966, 1975) Polymer Handbook Wiley, New York
24. Amog Y, Klein J (1985) J Coll Interf Sci 106:33
25. Hunter MJ, Warrick EL, Hyde JF, Currie CC (1946) J Am Chem Soc 68:2284
26. Hunt JM (1979) Petroleum Geochemistry and Geology, Freeman and Company, San Francisco, Ch 3
27. Varoqui R, Dejardin P (1977) J Chem Phys 66:4395
28. Kawaguchi M, Takahashi A (1980) J Polym Sci Polym Phys Ed 18:2069
29. Mijnlieff PF, Wiegel FW (1978) J Polym Sci Polym Phys Ed 16:245
30. Klein J, Luckham PF (1984) Nature 308:836

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