

### On the Role of Adsorption in the Drag Reduction Effect

At first glance, the concept of an adsorbed polymer layer as the dominant feature of the drag reduction mechanism is a thoroughly intriguing one. A number of investigators<sup>1-5</sup> have proposed such a model to account for the increased flow of fluids under turbulent conditions when trace amounts of linear high molecular weight polymers are added to fluids. However satisfying such a concept may be in a preliminary sense, it is perhaps somewhat suspect. In specific, it is extremely difficult to comprehend how a relative thin polymer layer on a surface can grossly affect the flow in a viscous sublayer which is several orders of magnitude greater in thickness, even if drag reduction is considered to be entirely a sublayer thickening effect.<sup>6,7</sup>

In the present work, adsorption, ellipsometric, and drag reduction experiments were run on aqueous solutions of several drag-reducing polymers in contact with a wide variety of substrates. The characteristics of the powdered adsorbents are shown in Table I. The adsorption of Polyox and polyacrylamide on these materials is indicated in Table II. The amount adsorbed was determined by analysis of the polymer concentration by either UV absorption or viscosity measurements. Having confirmed the adsorptive

TABLE I  
Some Characteristics of Powdered Adsorbents

Type	BET Surface area m <sup>2</sup> /g	Average diameter, μ	Cleaning procedure
Cabosil (silica)	150-200 <sup>a</sup>	0.015	muffle oven >500°C
Fractionated Pyrex <sup>a</sup>	~0.90 <sup>d</sup>	<44 <sup>b</sup>	muffle oven at 500°C
Stainless steel	>0.018 <sup>d</sup>	<44 <sup>b</sup>	Soxhleted 2 days with acetone, vacuum dried at 50°C

<sup>a</sup> Manufacturer's specifications.

<sup>b</sup> 325 mesh.

<sup>c</sup> Smaller particles removed by settling in water.

<sup>d</sup> BET kindly performed by Dr. V. R. Deitz

TABLE II  
Maximum Adsorption of Polymers on Cabosil, Pyrex, and  
Stainless-Steel Powders from Aqueous Solution

Polymer	pH	Adsorbent	Adsorbance	
			mg/g	mg/m <sup>2</sup>
Polyox (mol wt = $7 \times 10^6$ )	~5	fractionated Pyrex	≤0.9	≤1.0
Polyacrylamide (mol wt = $5-6 \times 10^6$ )	2.4 (HCl)	Cabosil	~60	~0.4
Polyacrylamide	~5	fractionated Pyrex	≤0.02	≤0.02
Polyacrylamide	~2 (HCl)	fractionated Pyrex	no detectable adsorption	
Polyacrylamide	~5	stainless steel	0.017-0.08	not accurate

TABLE III  
 Characteristics of Adsorbed Films from Ellipsometric Measurements<sup>a</sup>

Film concentration, mg/ml	RMS <sup>b</sup> thickness, Å repetitive	Adsorbance, mg/m <sup>2</sup>	Time, min
a. Polyacrylamide, 0.604 mg/ml H <sub>2</sub> O, Adsorbed Onto a Polished Stainless Steel Slide			
17.0	523	1.3	25
16.8	393	1.0	
13.3	620	1.2	75
15.2	687	1.6	
15.7	628	1.5	105
17.4	685	1.8	
14.3	767	1.7	138
16.4	736	1.8	
16.4	754	1.9	215
18.6	734	1.8	
20.2	769	2.3	overnight
17.6	744	2.0	
b. Polyacrylamide, 1.076 mg/ml H <sub>2</sub> O (pH 2.4), Adsorbed Onto Quartz			
144.6	81	1.8	overnight
150.1	79	1.8	
c. Polyox, 2.05 mg/g in 0.5 Molal MgSO <sub>4</sub> Solution, Adsorbed Onto Stainless Steel			
25.2	2089	7.9	50
d. Polyox, 0.4 and 1.3 mg/ml H <sub>2</sub> O, Adsorbed Onto Quartz			

No ellipsometric change was found for a duration of 4 days in the Polyox solution-quartz system. Hence, assuming Polyox adsorbs, it does so either in a very flat configuration ( $<50 \text{ \AA}$  for an adsorbance of  $\approx 1 \text{ mg/m}^2$ ), or the adsorbance is very low ( $<1 \text{ mg/m}^2$  for a  $50\text{-\AA}$  film) or both.

<sup>a</sup> The ellipsometric technique was checked out with a polystyrene cyclohexane solution, as is described in reference 13. The data represent single runs, and the main *qualitative* inference to be drawn from them is that drag reducing polymers can adsorb in a relatively flat conformation. The ellipsometric technique gives the refractive index and the thickness (based upon a homogeneous film) of the adsorbed film. From a knowledge of  $dn/dc$ , one can calculate the film concentration. From the film concentration and ellipsometric film thickness, one can calculate the adsorbance. The thickness presented in Table III, the RMS thickness is the ellipsometer thickness divided by 1.5, as is suggested in reference 8. Data, when given in pairs, represent the 95% confidence limits of the computer solutions of the Drude equations.

<sup>b</sup> RMS Thickness = ellipsometer thickness/1.5.

tendencies of the two drag-reducing polymers, ellipsometric measurements of adsorbed film thicknesses were then made on allied materials using an O. C. Rudolph and Sons Model 43702 ellipsometer. These data are listed in Table III, where the film depths are reported as root mean square (RMS) thicknesses based on the assumption of an exponential concentration in the polymer film.<sup>8</sup> For purposes of comparison, the drag reduction experiments which employed four inch disks of various materials are summarized in Table IV. The drag reduction equipment has been described elsewhere.<sup>9</sup>

Tables II-IV provide a basis for the following generalizations:

1. The adsorption of drag-reducing polymers on various materials is significant but lower than expected, with the exception of the acid PA/Cabosil system.

TABLE IV  
Summary of Drag Reduction Results

Experiment	Comments
Surface energy effects	none observed; same polymer solution gave 50% D.R. with steel, nylon, Teflon, and glass disks
Disk with adsorbed film placed in water	no D.R. observed
Disk cleanliness	no effect
Addition of salt	D.R. is decreased

2. The thickness of these adsorbed films tends to be very small, suggesting that the polymers lie in a flat configuration on the surface, in agreement with the results of other workers.<sup>10</sup>

3. The addition of  $MgSO_4$  greatly increases the film thickness, while it is well known that added salt decreases the observed drag reduction.<sup>11</sup>

4. Surface energy effects are unimportant, since disk composition and cleanliness had no effect on the observed drag reduction. Specifically, acid-cleaned or detergent-cleaned disks gave results identical to disks exposed to the laboratory environment. Detergent-cleaned low-energy surfaces such as Teflon gave the same results as acid-cleaned (hot nitric sulfuric acid solution) stainless steel.

In the light of these results and previously published work,<sup>12</sup> it is difficult to see how an adsorbed layer can perform a major role in the drag reduction mechanism. The concept of a viscous sublayer flow being influenced by an adsorbed layer several orders of magnitude smaller in thickness seems tenuous at best. In their explanation of an adsorbed layer model, Bryson, Arunachalan, and Fulford<sup>5</sup> have proposed that free-hanging loops of polymer molecules will reduce the flow in such a layer. However, it has been shown in the present work that such polymers apparently lie flat or nearly so with respect to the surface. Moreover, while the adsorbed film thickness of Polyox is significantly increased by the addition of salt, the drag reduction effect is correspondingly decreased. It must again be concluded, therefore, that an adsorbed polymer layer plays no more than a minor role (if any) in the drag reduction effect. A more complete report on the results reported here is available.<sup>13</sup>

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