

# **Surface Viscosity of Polydimethylsiloxane Monolayers**

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# Surface Viscosity of Polydimethylsiloxane Monolayers

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Abstract: The surface viscosities of a series of polydimethylsiloxanes were studied using a canal viscometer as well as a torsional surface viscometer. The siloxane monolayers investigated had molecular weights ranging from 520 to approximately 105,000 and included both the ethoxy and trimethyl end-blocked polymers. The surface viscosity of even the highest molecular weight polydimethylsiloxane monolayer was extremely low, below the limit of sensitivity of the canal viscometer, which is of the order of  $10^{-9}$  surface poise. This surface viscosity is remarkably low when compared with monolayers of other polymeric materials that have been studied at the water/air interface. Many of these polymers such as poly- $\epsilon$ -capramide (6-Nylon), the proteins, and synthetic polypeptides have given highly viscous, or viscoelastic, non-Newtonian films even at film pressures of only a few dynes/cm. The low surface viscosity of the siloxanes reflects the relatively low intermolecular cohesion that exists between adjacent siloxane chains in a monolayer. This low surface viscosity may in part explain the defoaming and antifoaming ability of the polydimethylsiloxane fluids.

## INTRODUCTION

Monomolecular films of many polymeric materials, such as poly- $\epsilon$ -capramide (6-Nylon) and synthetic polypeptides, adsorbed at the water/air interface are known to have high surface viscosities, even at film pressures as low as 1 or 2 dynes/cm (1-3). This is particularly true for protein monolayers, which often become plastic or viscoelastic as the film pressure increases (4-8). The high surface viscosity or viscoelasticity of these films has been attributed to the strong intermolecular cohesive forces, such as hydrogen bonding, that occur between adjacent molecules in the film. The rheological properties reported for films of a variety of synthetic polypeptides were similar to those of the natural proteins, the surface viscosities being high and generally non-Newtonian as the films were compressed (9-12). Studies have also been made of the viscoelastic properties of other synthetic polymer monolayers such as the various Nylons, polyvinylacetate (PVAc); polymethylacrylate (PMA), and poly(methyl methacrylate) (PMMA) (13-15). The Nylon monolayers were found to be highly viscous or viscoelastic at close packing, indicating a high degree of intermolecular cohesion. Motomura and Matuura (14) reported the surface viscosities of

the following polymers to be in the order PMMA > PMA > PVAc, the same order as the relative cohesive energies between monomers of the polymers, with the PVAc perhaps being slightly soluble.

Unlike the above polymer films, polyorgano-siloxanes should exhibit low intermolecular cohesion, and one would predict their surface viscosities to be extremely low. Monomolecular films of the siloxanes (or "silicones") have been spread at the water/air interface, and their surface behavior in terms of film pressure *vs* the area-per-molecule ( $F$  *vs*  $A$ ) and surface potential *vs* the area-per-molecule ( $\Delta V$  *vs*  $A$ ) have been discussed (16-19), but little has been reported regarding their rheological behavior. The viscosity of siloxane monolayers is of particular interest in view of their known proficiency as defoaming and antifoaming agents (18); however, the mechanism by which the silicone monolayers act as defoaming agents is still not known. The role of surface viscosity in determining the ability of many surface-active agents to stabilize foams is also not completely understood, although with foams stabilized by proteins the high surface viscosity appears to be a dominant stabilizing factor (20,21). On the other hand, many of the common defoaming agents such as 2-ethylhexanol or methylisobutylcarbinol will have very low surface viscosities. In addition to the viscosity effect, Ellison and Zisman (22) proposed that the defoaming

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ability of the siloxanes in both aqueous and non-aqueous systems is due to (a) the ability of silicone monolayers to adsorb at the liquid/gas interface and displace the previously adsorbed foam-stabilizing materials and (b) the inability of the silicone monolayers to increase the viscosity of the water/air or organic liquid/air interfaces.

In this study the rheological properties of a number of siloxane monolayers were investigated. The surface viscosities were determined with a canal viscometer when applicable, since the canal technique is capable of greater sensitivity and accuracy than those techniques based on the torsional behavior of a ring or disk suspended in the interface (23,24).

The canal viscometer is satisfactory at film pressures below the characteristic "plateaus" in the  $F$  vs  $A$  curves of siloxane monolayers. At higher film pressures, extending into the plateau region, the adsorbed molecules on each side of the canal will have quite different orientations and compressibilities, and it is difficult to assign an average viscosity to the film in the canal. Another disadvantage of the canal technique is the difficulty of correlating the surface viscosities with the various inflection points of the  $F$  vs  $A$  curves of the siloxanes, particularly in the plateau. For these reasons it was decided to use a torsional viscometer as well as the canal viscometer, especially at the higher film pressures.

## EXPERIMENTAL DETAILS

### Materials

Two series of well-defined polydimethylsiloxanes, kindly supplied by the Dow Corning Company, were available for this investigation, the ethoxy end-blocked compounds with the general formula  $C_2H_5O[Si(CH_3)_2O]_n C_2H_5$  and the trimethyl end-blocked series  $(CH_3)_3Si[OSi(CH_3)_2]_n OSi(CH_3)_3$ . Of these compounds the ethoxy end-blocked siloxanes having  $n = 4, 6, 8, 10, 14.5,$  and  $67$  and the trimethyl end-blocked compounds having  $n = 6, 10, 15,$  and  $43$  were studied. A phenylated siloxane from Dow Corning, DC 510, also was used in this study. Two samples of this phenylated compound, containing one phenyl group for every 20 methyl groups, were investigated, a 50-centistoke fluid and a 100-centistoke fluid. Compared with many

polymers, the molecular weights of these compounds are all rather low, the molecular weight of the  $n = 67$  ethoxy end-blocked siloxane being only about 5000. In order to study the surface viscosity of higher molecular weight silicones, it was necessary to go to the less well defined, higher bulk viscosity compounds. Dow Corning DC 210 (30,000 centistokes at 25°C) and Viscasil 100,000 (100,000 centistokes at 25°C) from the General Electric Company were selected as the higher molecular weight siloxanes, the average molecular weight of Viscasil 100,000 being estimated at about 105,000.

To remove surface-active impurities, the lower viscosity siloxane fluids were put through adsorption columns containing activated Florisil. Those silicones too viscous to flow readily through adsorption columns, however, were used as received. Spreading solutions of the siloxanes were prepared by dissolving known amounts of each compound in C.P. petroleum ether (b.p. 41-55°C). The petroleum ether was also percolated through activated Florisil. The spreading solutions were delivered to the water surface from Misco micro-pipets. In each case the substrate was triply distilled water, with an all-quartz apparatus being used for the final two distillations.

### Canal Viscometer

The canal surface viscometer used in this study was described in detail previously (25). Briefly, it employed a narrow, deep canal as suggested by Harkins and Nutting (23). The canal was formed from two glass microscope slides 7.5 cm long, 0.1 cm thick, and 1.6 cm wide. The slides were placed in a film balance trough so that the upper edges were exactly level with the free water surface. Only the upper edges of the slides were coated with paraffin; those portions of the slides remaining in contact with water were left hydrophilic to prevent slipping between the substrate water and the sides of the canal. The viscometer was constructed such that the canal width and alignment could be carefully controlled. The canal assembly was mounted in the middle of a Cenco hydrophil balance. A modified Cenco torsion head was used to measure the drop in film pressure between the ends of the canal, while a Wilhelmy-type tensiometer continuously monitored the film pressure of the monolayer at

one end of the canal. All film balance surfaces that came in contact with the substrate were made hydrophobic by coating with a thin layer of paraffin.

The procedure used to determine surface viscosity with the canal viscometer essentially involved measuring the amount of film passing through the canal in unit time with a given pressure difference between the ends of the canal. A monolayer was initially spread outside both ends of the canal and then compressed with the barriers until the film on one end registered a pressure  $F_1$  and the film on the other end a pressure  $F_2$ . The pressure differential along the canal was then  $\Delta F = F_1 - F_2$ , and the average film pressure in the canal was assumed to be  $(F_1 + F_2)/2$ . During the present investigation a pressure difference of 2 dynes/cm was routinely maintained along the canal.

For a canal of this design Harkins and Kirkwood (26) proposed that the rate of flow of film material through the canal is related to the absolute viscosity  $\eta$  of the monolayer by the equation

$$\eta = \frac{(F_1 - F_2)a^3}{12 l Q} - \frac{a \eta_0}{\pi}, \quad (1)$$

in which  $a$  is the width of the canal in centimeters,  $Q$  is the area in square centimeters of film flowing through the canal in 1 second,  $l$  is the length of the canal in centimeters, and  $\eta_0$  is the bulk viscosity of the aqueous substrate. These measurements were all carried out at  $20 \pm 0.2^\circ\text{C}$ .

### Torsional Surface Viscometer

The torsional viscometer was similar to many that have been reported in the literature (24,27, 28). It consisted of a hollow sharp-edged brass cylinder 1.750 cm in diameter suspended from a torsion wire 41.8 cm long and 0.010 cm in diameter. The sides of the cylinder were coated with a fluorocarbon polymer (29) to prevent erratic wetting of the cylinder by the substrate. In practice the cylinder height was adjusted so that the ring formed by its bottom edge just touched the water surface. The moment of inertia of the cylinder was 44.92 g-cm<sup>2</sup> but could be increased to more than 150 g-cm<sup>2</sup> by adding circular disks of known moment of inertia. The outer wall of the cylinder was calibrated, in degrees, permitting

the periodic motion to be determined using a cathetometer telescope.

The torsional viscometer was mounted in a Langmuir-Adam-type film balance, which had a Pyrex glass trough 12 cm wide, 74 cm long, and 0.5 cm deep, with the rim lightly coated with paraffin. The film balance was equipped with a modified Cenco du Nuoy torsion head that was sensitive to changes in film pressure of 0.05 dynes/cm. The viscometer cylinder was approximately 6 cm from the torsion head and about 5 cm from each side of the trough. This film balance was also used to determine the  $F$  vs  $A$  curves of the siloxane monolayers prior to the viscosity determinations.

Surface viscosity was determined by measuring the logarithmic decrement of the torsional oscillation of the ring at a clean water surface and comparing it with a similar measurement for the monolayer covered surfaces. The surface viscosity  $\eta$  was calculated using the equation (30)

$$\eta = 2H_s I_r \left( \frac{\lambda}{T} - \frac{\lambda_0}{T_0} \right), \quad (2)$$

where  $T$  is the period of oscillation (the subscript zero refers to the clean water surface),  $\lambda$  is the natural logarithmic decrement of the damped oscillations,  $I_r$  is the moment of inertia of the oscillating ring assembly, and  $H_s$  is an apparatus constant dependent upon the geometry of the equipment. During most of the experiments  $I_r$  was 114.47 g-cm<sup>2</sup> and  $T$  was 16.8 sec. The period of oscillation was the same for both clean and monolayer-covered surfaces. The apparatus constant  $H_s$  is given by the equation

$$H_s = \frac{1}{4\pi} \left( \frac{1}{r_1^2} - \frac{1}{r_2^2} \right), \quad (3)$$

where  $r_1$  is the radius of the ring and  $r_2$  is the effective radius of the film trough. In the present experiments  $H_s$  is 0.0237 cm<sup>-2</sup>. To determine  $\lambda$ , the natural logarithm of the peak amplitudes of the oscillations was plotted against the number of oscillations, the slope of the line being the logarithmic decrement. In this study at least 10 periodic oscillations were plotted for each  $\lambda$  determination. As required by theory the logarithmic decrement was found to be independent of the amplitude of the oscillations. All measurements with this apparatus were carried out in a constant-temperature

room at  $25 \pm 0.5^\circ\text{C}$ . The apparatus was further enclosed in a glass and aluminum box with exterior controls.

## RESULTS

### Isotherms of Film Pressure *vs* Area/Molecule

Isotherms of  $F$  *vs*  $A$  were determined on triply distilled water for each of the siloxane monolayers studied. The data shown in Fig. 1 are for a series of trimethyl end-blocked polydimethylsiloxanes but are typical of the results obtained with each of the siloxanes. Each  $F$  *vs*  $A$  curve was repeated at least three times, the variation between the separate runs being less than  $\pm 0.2$  dyne/cm at any area/molecule. These curves are also in agreement with those previously reported in the literature for similar siloxanes (16-19). Monolayers of the low molecular weight siloxanes ( $n < 6$ ) were not stable with time and appeared to be either slightly soluble or volatile. Also they did not show the plateau in the  $F$  *vs*  $A$  curve, or the inflection points that are characteristic of the higher molecular weight siloxanes.

### Surface Viscosity by Canal Viscometer

Use of the canal viscometer was limited to siloxane monolayers having an average film pressure in the canal of 1 to 7 dynes/cm. Because of instability of monolayers of the low molecular weight siloxanes, the method was also limited to those siloxanes where  $n \geq 8$ . Surface viscosities were determined at several canal widths up to 0.190 cm as an independent check on the technique. With the narrower canals, less than about 0.092 cm, there was a significant scatter in the results, perhaps due to frequent blocking of the narrow canal by dust particles and other small obstructions.

For every compound studied, at a given canal width and film pressure, at least 3 independent determinations of the film flow rate were made, and every determination was the average of at least 5 consecutive measurements. It was found that at a given canal width the film flow rate  $Q$  was independent of the molecular weight of the polydimethylsiloxane (with  $n \geq 8$ ) and independent of film pressure, at least up to 7 dynes/cm. The combined film flow rate data for all siloxanes

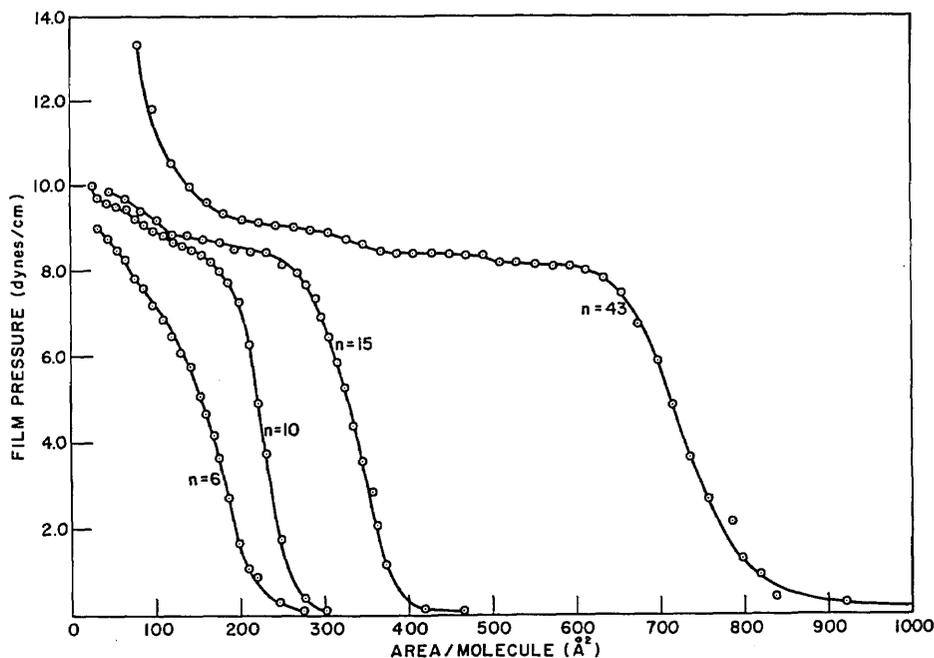


Fig. 1 — Film pressure *vs* area/molecule for polydimethylsiloxanes of the type  $(\text{CH}_3)_3\text{Si}[\text{O Si}(\text{CH}_3)_2]_n\text{OSi}(\text{CH}_3)_3$  on distilled water

TABLE I  
 Combined Canal Viscometer Data for all Polydimethylsiloxanes at all  
 Average Film Pressures Studied (Data Given for Five Canal Widths)

(1) Canal Width (cm)	(2) Film Flow Rate, $Q$ (cm <sup>2</sup> /sec)	(3) Standard Deviation of Film Flow Rate	(4) Uncorrected Surface Viscosity (surface poise)	(5) Standard Deviation of Uncorrected Surface Viscosity	(6) Correction Factor from Eq. (1)	(7) Corrected Surface Viscosity: (4)-(6) (surface poise)
0.092	0.0565	0.0020	0.000295	0.000015	0.000293	+0.000002
0.117	0.0946	0.0039	0.000370	0.000015	0.000373	-0.000003
0.141	0.140	0.006	0.000446	0.000019	0.000449	-0.000003
0.166	0.190	0.008	0.000526	0.000021	0.000529	-0.000003
0.190	0.248	0.011	0.000625	0.000028	0.000605	+0.000020

at all film pressures studied gave more than 100 independent determinations of  $Q$  at each canal width. The average film flow rates and the standard deviations at each canal width are listed in Table I. In column 4 of Table I are given the average uncorrected surface viscosities of the siloxane monolayers as calculated from the first term in Eq. (1), followed by their standard deviations in column 5. In column 6 the correction factors are given as calculated from the second term of Eq. (1). It is apparent that the surface viscosities of the polydimethylsiloxanes are determined as the difference between the two relatively large numbers. The differences between columns 4 and 6, or the corrected surface viscosities, are seen to be extremely small, of the order of  $10^{-5}$  surface poise or less. In each case the corrected surface viscosities are less than the standard deviations in column 5. It is apparent then that the true surface viscosities of polydimethylsiloxane monolayers will be extremely small, probably less than  $10^{-5}$  surface poise. The surface viscosities of those slightly phenylated siloxanes studied were not significantly different from the polydimethylsiloxanes. Surface viscosities were not reported for the more highly phenylated siloxanes, as well-defined samples of these materials were not available.

#### Surface Viscosity by Torsional Viscometer

The torsional viscometer was used to determine primarily whether the siloxane monolayers

developed an appreciable viscosity at high film pressures and further whether any of the inflection points in the  $F$  vs  $A$  curve gave corresponding changes in surface viscosity. Fewer of the siloxanes were studied by this technique than by the canal viscometer, the experiments being limited primarily to those compounds having higher molecular weights. For each compound studied a plot of the natural logarithm of the peak amplitude of each oscillation vs the number of oscillations was constructed, as shown in Fig. 2 for the 30,000-centistoke polydimethylsiloxane. The slope of this plot gives  $\lambda$ , the logarithmic decrement of the torsional oscillation. In Fig. 2 the logarithmic decrement  $\lambda$  varied from 0.0602 to 0.0615, with no obvious trend being observed in going from a clean water surface to a film pressure of 10 dynes/cm. The difference of 0.0013 between the extreme values of  $\lambda$  is typical of the data for the other siloxanes, the maximum difference being less than 0.0020 in all cases. The insensitiveness of the measurements can be seen in Fig. 3, where the natural logarithmic decrement for several of the siloxanes are plotted against the film pressure of the monolayers. The solid lines correspond to the value of  $\lambda_0$  for a clean water surface, and the points correspond to the logarithmic decrements determined in the presence of the monolayers. As the values of  $\lambda_0$  are within the extremes of  $\lambda$  for the monolayers, it is apparent that the logarithmic damping of the oscillating cylinder on clean water is not significantly different from that on a monolayer covered surface. Therefore, the

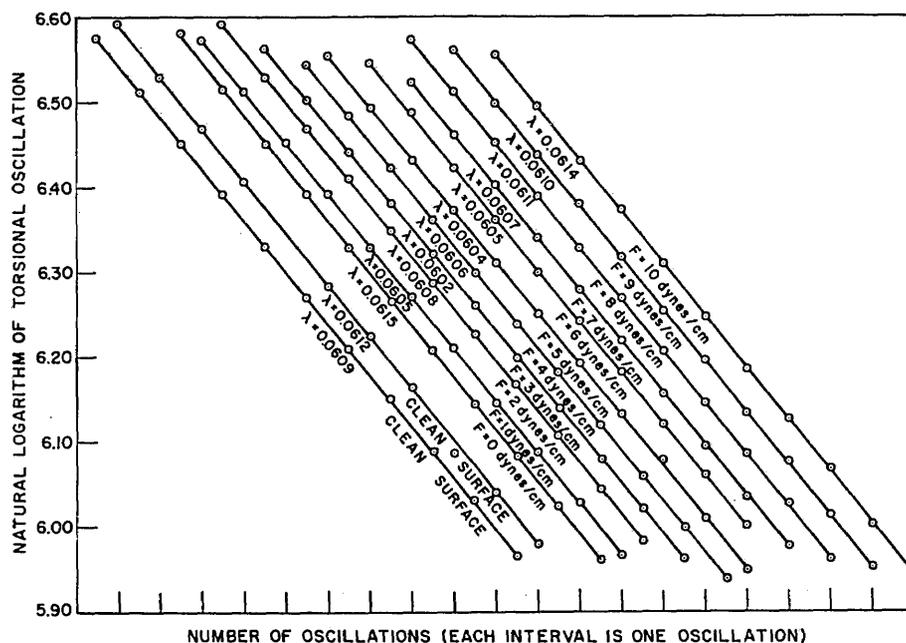


Fig. 2 — Natural logarithm of the peak amplitudes of the torsional oscillations *vs* the number of oscillations for monolayers of a polydimethylsiloxane (30,000 centistokes at 25°C). The slope gives  $\lambda$ , the logarithmic decrement of the torsional oscillation.

surface viscosities of polydimethylsiloxane monolayers are certainly below the sensitivity limit of this torsional viscometer, even at film pressures corresponding to the collapse pressures of the monolayers. A difference of 0.020 in the logarithmic decrement corresponds to a surface viscosity difference of 0.00065 surface poise, which may be taken as the sensitivity limit of this torsional viscometer. The surface viscosities of the siloxane monolayers are certainly well below this value.

### DISCUSSION

The results of this study show that the surface viscosities of the polydimethylsiloxanes are certainly below the limit of detectability of the surface viscometers used and are exceptionally low for polymers adsorbed at the water/air interface. Based on the results of the canal viscometer, their viscosities are probably below  $10^{-5}$  surface poise. Even when the monolayers are highly compressed and begin to show visible evidence of film collapse, there is no measurable surface viscosity. A surface viscosity of this low order of magnitude seems quite remarkable

for a long-chain polymeric material, particularly one having a molecular weight as high as about 105,000. This must reflect the low intermolecular cohesion that is present in siloxane films, compared with monolayers of proteins and certain linear synthetic organic polymers (14). Therefore, it can be concluded that the ability of siloxane polymers to act as defoaming and antifoaming agents is undoubtedly related to their unusually low surface viscosities and their ability to displace the less strongly adsorbed foam-stabilizing materials.

Garrett and Zisman (31) have reported another remarkable and interesting property of the linear polydimethylsiloxane films, namely, their remarkable effect on the so-called capillary waves on water. They reported that these films can be very effective in damping the capillary waves, but only at certain states of compression of the monolayer. These siloxanes gave large "damping coefficient" peaks at areas/molecule corresponding to (a) the initial rapid increase in film pressure with decreasing area, (b) the beginning of the plateau region of the  $F$  vs  $A$  curve, (c) the inflection point on the plateau, and (d) the approach to closest packing of the

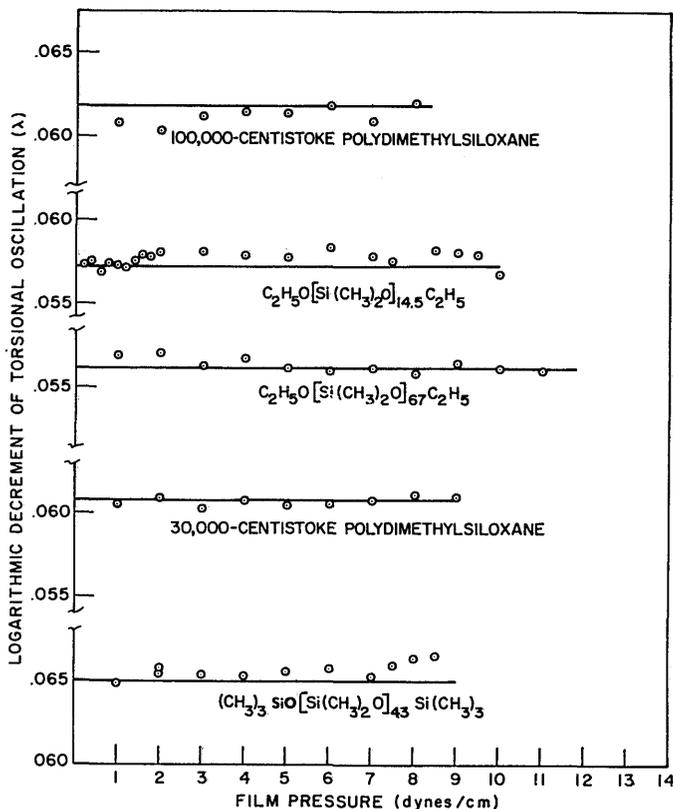


Fig. 3 — The logarithmic decrements of torsional oscillation ( $\lambda$ ) of several polydimethylsiloxanes as a function of the film pressure of the monolayer. The solid line corresponds to  $\lambda_0$ , the logarithmic decrement for clean water.

adsorbed molecules. Between these peaks the monolayers had only a small effect on the amplitude of the capillary waves. It is interesting that surface viscosity shows no such correlation with structure of the monolayer, or that such a remarkable damping of capillary waves can occur at all in the absence of a measurable surface viscosity.

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	ROLE	WT	ROLE	WT	ROLE	WT
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