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SOME SURFACE-ACTIVE PROPERTIES OF THE LINEAR POLYORGANOSILOXANES - PART I

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ABSTRACT

A study has been made of the densities, the surface tensions and their temperature coefficients, the interfacial tensions against water, the spreading pressures and the force-area and potential-area relations of monolayers of various types of linear polyorganosiloxanes on water.

The McLeod constants and parachors have been calculated and their application to the type analysis of the "silicones" is discussed. Relations have been found between the "critical" spreading pressure, the spreading coefficient, and the viscosity. The study of the force-area curves revealed that the polymethylsiloxanes and the related polymers containing a small proportion of phenyl substituents are able to coil reversibly into helices made up of six monomers per turn. At low film pressures each helix uncoils and the molecule adsorbs with the long axis in the water. The length of the helix increases with the temperature. The potential-area changes with molecular packing were unusual. The electric moment per monomer has been obtained and its significance is briefly discussed. Conclusions relative to the molecular structures in thin films have been carried over to the three-dimensional liquid state. It is shown that a qualitative explanation can be given of the variation with substituents in the viscosity indices of the different linear polyorganosiloxanes and of the unusually high values of the methyl-substituted compounds.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

This study was undertaken under Problem Number 32C26-01 entitled "Investigation of Oil Additives with Particular Reference to Adsorption-Desorption Equilibrium of Additive Agents at the Oil-Metal and Oil-Water Interfaces".

SOME SURFACE-ACTIVE PROPERTIES OF THE LINEAR POLYORGANOSILOXANES - PART I

INTRODUCTION

Many of the physical and chemical properties of the polyorganosiloxanes (or "silicones") have been described recently.* Relatively few data have appeared concerning the surface-active properties, and their relation to molecular structure. This discussion deals with some of the properties of the available polyorganosiloxane films when adsorbed at the gas-silicone and water-silicone interfaces. Part II, to be published, will be concerned with adsorption phenomena at the interface between aqueous solutions and silicones.

EXPERIMENTAL

Materials and Apparatus

The linear polymethylsiloxanes from the dimer to the heptadecamer were carefully purified compounds having trimethylsiloxy end groups. Many of the properties of the dimer through the octamer have been described by Hunter et al.† The DC 500 series fluids are commercial mixtures of homologous linear polymethylsiloxanes, those under 5 centistokes (cstks) in viscosity apparently being distillation cuts. The samples of this series having viscosities lower than 5 cstks comprised a small range of molecular weights approaching pure compounds at the lowest viscosities (0.65, 1.0 and 1.5 cstks). This is evidenced by the close agreement of the surface tensions and densities with those measured for the linear dimer, trimer and tetramer. The polyethylsiloxanes and polymethylphenylsiloxanes used are producers' samples from pilot plant batches of mixed homologous compounds. The type classifications of these fluids given in Table I are based on the analyses of this laboratory, and particularly upon the results from infrared absorption studies. Almost all of the measurements were made in a constant temperature room held at 20 ± 0.2°C. The relative humidity was held between 50 and 60 percent. A Cenco-Du Nouy interfacial tensiometer was used for measuring the surface tensions of the materials which were available in sufficient quantity, the usual corrections‡ being applied. The surface tensions of the rarer materials and all the interfacial tensions were measured with a drop-weight

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* Baker, E. B., Barry, A. J., and Hunter, M. J., Ind. Eng. Chem. 38, 1117 (1946); Brophy, J. E., Militz, R. O., and Zisman, W. A., Trans. A.S.M.E., May 1946; Fitzsimmons, V. J., Pickett, D. L., Militz, R. O., and Zisman, W. A., Trans. A.S.M.E., May 1946; Hunter, M. J., Hyde, J. F., Warrick, E. L., and Fletcher, H. J., J. Am. Chem. Soc. 68, 667 (1946); Hunter, M. J., Warrick, E. L., Hyde, J. F., and Currie, C. C., J. Am. Chem. Soc. 68, 2284 (1946); Hurd, C. B., J. Am. Chem. Soc. 68, 364 (1946); Patnode, W., and Wilcock, D. F., J. Am. Chem. Soc. 68, 358 (1946); Sauer, R. O., and Mead, D. J., J. Am. Chem. Soc. 68, 1794 (1946); Sullivan, M. V., Wolfe, J. K., and Zisman, W. A., "The Flammability of the Higher Boiling Liquids and Their Mists", Ind. Eng. Chem., (In Press); Wilcock, D. F., J. Am. Chem. Soc. 68, 691 (1946).

† Hunter, M. J., Warrick, E. L., Hyde, J. F., and Currie, C. C., J. Am. Chem. Soc. 68, 2284 (1946).

‡ Harkins, W. D., and Jordon, H. F., J. Am. Chem. Soc. 52, 1751 (1930).

apparatus, and the appropriate corrections* were made. The measurements on the same materials using both instruments agreed within 0.1 dynes/cm.

TABLE I

Type Classification of the Polyorganosiloxanes Studied

Identification	Viscosity cstks at 25°C	Organic Substituents On Terminal Si Atoms	Organic Substituents On Other Si Atoms	Estimated Ratio* phenyl/methyl
Linear Polymethyl-siloxanes				
DC 500	All Visc.	Trimethyl	Methyl	0
Linear Polyethyl-siloxanes				
A1	13	Triethyl	Ethyl	0
A2	50	"	"	0
A3	158	"	"	0
Linear Polymethyl‡ phenylsiloxanes				
B1	3.5	1 Phenyl 2 Methyl		0.60†
B2	27	Trimethyl	Methyl - Phenyl	0.63
B3	50	"	" "	0.14
B4	50	No Trimethyl ‡	" "	0.53
B5	102	Trimethyl	" "	0.49

Note: These type classifications are approximate and do not completely exclude the presence of other siloxane structures.

* A rough estimate based on the ratio of intensities of infrared absorption maxima.

† Here the actual ratio of phenyl to methyl groups is 0.5.

‡ Probably terminal group has methyl and phenyl substitution.

The drop-weight apparatus consisted of a 1-ml Becton-Dickinson hypodermic syringe, the plunger of which was advanced by a micrometer screw. This made it possible to measure the expelled volume of liquid to ± 0.00008 ml. About 90 percent of the drop was formed by manually advancing the screw, and the remainder was allowed to form by driving the micrometer screw through a rubber coupling with a geared-down synchronous motor rotating one revolution in five minutes. This device expelled the liquid at the rate of 0.00003 ml/sec. The drive motor could be stopped in a fraction of a second after the drop fell. The dropping tips, which were made of platinum ground to fit the taper of the syringe, had diameters of 4, 2 and 0.75 mm measured to ± 0.0025 mm with a micrometer caliper. Densities were measured in 10-ml Sprengel tubes thermostatted at 20.00° ± 0.05° C.

The Langmuir film balance used in the majority of the experiments consisted of a stainless steel trough which was 1.3 cm deep, 14 cm wide, 65 cm long on the working side of the float and 20 cm long on the other side. The torsion head used was taken from a Cenco "Hydrophil Balance" fitted with a steel torsion wire requiring a twist of 6 degrees to exert a force of 1 dyne/cm at the float. The mica float was fastened to the trough with strips of annealed platinum 3 mm wide and 0.0001 in. thick. For experiments on the effect of aqueous ions and variations in the pH, a Pyrex trough approximately 15 cm wide, 68 cm long and 5 cm deep was used with a specially made torsion head fitted with a wire requiring a twist of 5 degrees to produce a force of 1 dyne/cm at the float. Film potential measurements were made with the vibrating electrode method of Zisman† using an electrically driven gold electrode 4 cm in diameter held approximately 1.5 mm above the water, a small Rubicon potentiometer, and a cathode-ray oscillograph (instead of a telephone) to detect the null point. The direct electrical contact with the water in the film balance was made by an immersed gold plate. Such potentials were easily and rapidly measured to ±5 millivolts. A precision of ±2 millivolts could be obtained when required by decreasing the separation of the vibrating electrode and the water.

It was essential to remove any traces of more surface-active compounds present as impurities by percolating each fluid through a long, narrow column packed with a suitable

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* Harkins, W.D., and Brown, F.E., J. Am. Chem. Soc. 41, 499 (1919).

† Yamins, H.G., and Zisman, W.A., J. Chem. Phys. 1, 656 (1933); Zisman, W.A., Rev. Sci. Instr. 3, 367 (1932).

TABLE II

The Surface Tensions, Interfacial Tensions Against Water, Densities, McLeod Constants and Parachors For Some Linear Polymethylsiloxanes (all measurements at 20°C)

Substance	Surface Tension Dynes/cm	Interfacial Tensions Against Water Dynes/cm	Density 20°/4°	McLeod Constant	Parachor	Parachor for Silicon
Pure Compounds						
Dimer	15.7		.7636	2.608	423	33.3
Trimer	16.96		.8200	2.475	585	32.1
Tetramer	17.60		.8536	2.400	745	31.1
Pentamer	18.10		.8755	2.356	908	30.6
Hexamer	18.45		.8910	2.326	1067	30.3
Heptamer	18.60		.911*	2.280*	1215*	28.2*
Octamer	18.82		.913*	2.281*	1385*	29.3*
Nonamer	19.24	37.0†	.9173	2.283	1554	30.3
Dodecamer	19.56	30.4†	.9314	2.258	2840	30.1
Heptadecamer	19.87	27.3†	.9428	2.239	2852	30.2
DC 500 Series						
0.65 cstks ‡	15.7	39.9	.7631	2.608		
1.0 "	16.8	42.5	.8199	2.469		
1.5 "	17.5	42.4	.8538	2.395		
3.0 "	18.5	40.0	.8939	2.319		
5.0 "	19.0	42.2	.9177	2.291		
10 "	19.4	39.9	.9392	2.234		
35 "	19.9	43.1	.9560	2.214		
56 "	20.2		.9643	2.202		
70 "	20.3		.9683	2.196		

* These values are approximate

† Unpercolated

‡ All viscosities at 25°C

selective absorbent. The "equilibrium" spreading pressures of the DC 500 fluids (discussed below) were found to be decreased permanently by this procedure and were used to indicate the relative effectiveness of removal of adsorbable impurities by the various adsorbents tried. As "Florisil" was the most effective of the adsorbents tested, it was chosen for use in purifying all of the silicones discussed here.

The Gas-Silicone Interface

The surface tensions in air are given in Tables II and III. No change exceeding a few tenths percent was found in the densities or surface tensions due to percolation. When surface tension was plotted against density, a linear graph was obtained for all of the polymethylsiloxanes of Table II. The data for all of the ethyl- and phenyl-substituted polymers fell well off the line, and they did not lie on any other straight line. This is to be expected since these polymers were not homologous. These surface tensions and especially those of the polymethylsiloxanes are very low for materials of such densities and boiling points. It is illuminating to note that the data for the series of normal aliphatic hydrocarbons lie on a linear curve which is displaced considerably from the curve for the polymethylsiloxanes. The silicone fluids when at room temperature dissolve about 25 percent of their volume of air. A series of surface tension measurements were made in a helium atmosphere after stripping the air from the fluids by evacuation and subsequent bubbling of helium through them. However, the surface tensions were found to be the same as in air.

The corrected surface tensions and densities in air at several temperatures, of all of the linear polyorganosiloxanes studied, are given in Table III. A more extended range of temperatures was used in the measurements on the 35 cstks DC 500 fluid, and the surface tension was found to change

TABLE III

Effect of Temperature on Surface Tension and Density of Various Polyorganosiloxanes

Fluid and Viscosity at 25°C	Temp. C°	Density t°/4°	Surface Tension	Coefficient of cubical Expansion x 10^3	$-\frac{d\gamma}{dt}$
Linear Polymethylsiloxanes					
Heptadecamer	20	0.9428	19.9	1.07	0.067
	35	0.9283	18.9		
DC 500-35 cstks	5	0.9689	21.10		
	10	0.9646	20.65		
	15	0.9602	20.38	1.00	0.067
	20	0.9557	20.00		
	25	0.9514	19.67		
	30	0.9469	19.35		
	35	0.9425	19.00		
Linear Polyethylsiloxanes					
A1 - 13 cstks	20	0.9535	23.3	0.87	0.060
	35	0.9418	22.4		
A2 - 50 cstks	20	0.9909	23.7	0.80	0.060
	35	0.9795	22.8		
A3 - 158 cstks	20	0.9941	25.7	0.67	0.073
	35	0.9840	24.6		
Linear Polymethylphenylsiloxanes					
B1 - 3.5 cstks	20	0.9809	29.6	0.87	0.080
	35	0.9686	28.4		
B2 - 27 cstks	20	1.0735	28.6	0.72	0.080
	35	1.0612	27.4		
B3 - 50 cstks	20	0.9955	22.2	0.93	0.12
	35	0.9827	20.4		
B4 - 50 cstks	20	1.0704	27.2	0.69	0.11
	35	1.0586	25.5		
B5 - 102 cstks	20	1.0787	26.1	0.71	0.11
	35	1.0665	24.4		

linearly with the centigrade temperature as follows:

$$15\,\gamma = 320 - t \qquad (1)$$

The McLeod constant for this material is 2.213 ± 0.002. The Eötvös constant was also calculated using the data on the polymethylsiloxane heptadecamer. The resulting value of 3.6 is much higher than the "normal" value of 2.1. Fluid B1 was assumed to be a phenyl-substituted dimer as indicated in Table I. The Eötvös constant calculated on this basis is 2.8. It is usually considered that a high Eötvös constant is indicative of a linear molecular structure, and this is obviously true here.

Sauer* has derived the group and bond refractions of a wide variety of organosilicon fluids and showed they can be used for determining the average composition of the polymethylsiloxanes. A more limited, though similar, analysis employing the atomic parachors was made and used by this Laboratory during the war for the identification of silicones. An example may be given for a linear polyorganosiloxane containing only methyl and ethyl group substituents. If no other groups are present, and m and e are the ratios of the number of methyl and ethyl groups to the number of silicone atoms n, the polymer may be represented as follows:

$$(CH_3)_m\ (C_2H_5)_e\ Si\ O_{\left(\frac{4-(e+m)}{2}\right)} \qquad (2)$$

Assuming aduitivity of the parachors, the specific parachor, p is then:

$$p = \frac{mP_{CH_3} + eP_{C_2H_5} + P_{Si} + \frac{1}{2}\,[4-(e+m)]\,P_O}{mM_{CR_3} + eM_{C_2H_5} + M_{Si} + \frac{1}{2}\,[4-(e+m)]\,M_O} \qquad (3)$$

where P and M refer to the group or atomic parachors and weights, respectively. Using Sugden's figures† for the parachors of CH_2, CH_3, O, and the authors' figure of 30.2 for Silicon, the expression reduces to:

$$p = \frac{46.1m + 85.1e + 70.2}{7.03m + 21.06e + 60.06} \qquad (4)$$

When e = 0 $$m = \frac{p - 1.169}{0.7676 - 0.1170p}. \qquad (5)$$

Since $$m = \frac{2 + 2n}{n}\ , \qquad (6)$$

relations (5) and (6) may be used to calculate n as well as the molecular weight of a linear polymethylsiloxane. It must be noted, however, that as the molecular weight becomes large, m approaches 2 as a limit and p changes very slowly. This makes it difficult to compute accurately the mass of a high molecular-weight polymer.

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* Sauer, R. O., J. Am. Chem. Soc. 68, 954 (1946).

† Sugden, S., and Wilkins, H., J. Chem. Soc., 126 (1931); Sugden, S., The Parachor and Valency, Alfred A. Knopf (1930).

The values for the methyl/silicon ratio are high when calculated using Sugden's early value* of the parachor of silicon of 27.8. Hunter et al† concluded that in four of the low molecular-weight cyclic polymethylsiloxanes the parachor of silicon varied between 25.8 and 27.1. Hunter and another group of workers‡ recently reported surface tension and density data for some linear polymethylsiloxanes. From these data the parachors have been computed for silicon and were found to vary from 27.8 to 31.1. Data of the authors are closer to the latter, the parachor for silicon becoming constant at 30.2 for linear polymethylsiloxanes containing more than 5 silicon atoms in the molecule. Equations (5) and (6) appear to discriminate the chain length satisfactorily up to the heptadecamer.

The Distilled Water-Silicone Interface

When in two non-miscible liquids $\gamma_B > \gamma_A + \gamma_{AB}$, liquid A will spread on liquid B. The indicative quantity $\gamma_B - (\gamma_A + \gamma_{AB})$ has been called the initial spreading coefficient§. Washburn and Keim** , employing a convenient and rapid hydrophil film-balance method, have shown experimentally that this coefficient is equal to the equilibrium spreading pressure for a number of liquid organic compounds on water. Their method was used in this study with eicosyl alcohol serving as the "piston film" material. Preliminary trials showed that there was no single pressure at which a bulk lens of a polymethylsiloxane fluid was in equilibrium with a monolayer of the same substance. However, two pressures which the authors call "critical spreading pressures" could be observed experimentally: (a) a pressure S_2 at which a visibly thick droplet changed in size considerably with a small decrease in pressure; (b) a pressure S_1, which was 0.1 to 0.5 dynes/cm lower than S_2, where a thin disc showing interference colors increased or decreased in size rapidly with little change in pressure. Pressure S_1 was the more reproducible and represented a highly compressible and reversible state of the silicone film as confirmed by the force-area studies described in the next section. Pressure S_2, which is the pressure necessary to reduce the thin film to bulk liquid, increased rapidly with each expansion and recontraction of a given droplet, until the pressure was several dynes/cm above the value for the first expansion and contraction. This phenomenon was evidenced in the force-area curves given below and will be discussed again in that connection.

Table IV shows the effect of the various adsorbents on the value of S_1 for the 70 cstks DC 500 fluid. Of all the adsorbents tried "Florisil" produced the largest effect. After the first percolation of each silicone sample a yellow ring was left at the top of the column of adsorbent. This yellow material had an aromatic odor but no attempt was made to identify it. No such residue was left after the second percolation. On simply standing in contact with the atmosphere in a clean pyrex container, the silicone fluids developed higher values of S_1 than were exhibited by freshly percolated materials, the greatest change taking place in the first few hours. However, the critical pressure S_1 did not revert back to the values for the unpercolated fluids. For example, in several experiments, the fluid was taken directly from the delivery tube of the adsorption column, and S_1 was found to be as small as 7.9 dynes/cm. Within two hours after percolation the same batch of silicone was tested and

* Sugden, S., and Wilkins, H., J. Chem. Soc., 126 (1931); Sugden, S., The Parachor and Valency, Alfred A. Knopf (1930).

† Hunter, M. J., Hyde, J. F., Warrick, E. L., and Fletcher, H. J., J. Am. Chem. Soc. 68, 667 (1946).

‡ Hunter, M. J., Warrick, E. L., Hyde, J. F., and Currie, C. C., J. Am. Chem. Soc. 68, 2284 (1946).

§ Harkins, W. D., and Feldman, A., J. Am. Chem. Soc. 44, 2665 (1922).

** Washburn, E. R., and Keim, C. P., J. Am. Chem. Soc. 62, 1747 (1940).

S_1 had become about 10.0 dynes/cm. The critical pressure S_1 was carefully measured two hours and also 50 days after percolation for the series of DC 500 fluids of Table V. These fluids were stored the entire time after percolation in clean stoppered pyrex bottles. In each instance nearly all of the increase in S_1 of 0.2 to 1.0 dynes/cm occurred in the first few hours. From Table V it will be noted that S_1 increased with decreasing molecular weight (or viscosity). When the logarithm of the viscosity at 25°C was plotted against the critical pressure S_1, a straight line was obtained provided the graph points for the fluids of 3.0 cstks or less were disregarded. This is not unreasonable since it is shown later that the silicones below the octamer (4 cstks) do not have critical spreading pressures but may have an equilibrium spreading pressure.

TABLE IV

The Critical Spreading Pressure of a Polymethylsiloxane After Percolation Through Various Adsorbents

Adsorbent	Spreading Pressure of 70 cstks DC 500 Fluid After Percolation
None	15.0 dynes/cm
Filter paper	14.9
Charcoal (granular "Nuchar")	14.3
Alumina (Aluminum Ore Co.)	12.7
Silica gel (Davison Chem. Co.)	13.9
Florisil 100/200 mesh (Floridin Co.)	9.6
" 40/60 " " "	10.1

Note: The adsorbents were activated by a four hour baking at 250°C. They were used immediately after cooling to room temperature.

TABLE V

Critical Spreading Pressure S_1 of Various Polymethylsiloxanes DC 500 Fluids Percolated Through Florisil

Viscosity (cstks) at 25° C Column 1	Critical Spreading Pressure dynes/cm at 20°C		
	Observed	Calculated Spreading Coefficient	
	S_1 Measured 2 Hours after percolation Column 2	From Data of Table II (S_{AB}) Column 3	From Data of Table II and Interfacial Tension of 42.5 Column 4
0.65	14.6?	17.2	14.6
1.0	13.0?	13.4	13.5
1.5	13.2	12.9	12.8
3.0	13.3	14.3	11.8
5.0	12.0	11.6	11.3
10.	11.6	13.4	10.9
35.	10.5	9.6	10.2
56.	10.2		10.1
70.	10.0		9.9

The spreading pressures of the silicones are greater than those of all but the very volatile hydrocarbons but are less than those of most hydrocarbon derivatives containing a single hydrophilic substituent. The polyethylsiloxane fluid (A2) showed no evidence of possessing such a critical spreading pressure. The phenyl-substituted compounds showed a critical pressure similar to S_1 but it was less well-defined depending on the degree of phenyl substitution.

The interfacial tensions for the most part were more difficult to measure because of the small density differences between the silicones and water. It was impossible to use the ring method because even in containers 15 cm in diameter, the interface was appreciably curved at the center. Some difficulty was experienced with the drop-weight method because the drop became inconveniently large. Therefore, no measurements were made of the interfacial tensions of the silicones having viscosities over 35 cstks. The interfacial tensions measured are listed in Table II and are uncertain to ± 0.5 dynes/cm. The best value is 42.5 dynes/cm. Percolation caused changes in the interfacial tensions, as would be expected from the fact that the surface tensions were not affected while the spreading pressures were. For example, the interfacial tension of the 35-cstk DC 500 fluid was 36.9 dynes/cm when unpercolated and 43.1 dynes/cm after percolation. Allowing the silicone to stand after percolation for lengths of time up to several hours did not seem to affect the interfacial tension although the experimental uncertainty in the measurement may have obscured minor effects.

It is interesting to calculate the initial spreading coefficient S_{AB} of Harkins and Feldman* from the surface and interfacial tension data of Table II. In Column 3 of Table V will be found the values of S_{AB} calculated from the observed surface and interfacial tension of Table II, while in Column 4 are the results when the best interfacial tension of 42.5 dynes/cm is used instead. The surface tension of water at 20° C was taken to be 72.8

* Harkins, W. D., and Feldman, A., J. Am. Chem. Soc. 44, 2665 (1922).

dynes/cm. The agreement of Columns 2 and 4 is as good as could be expected for all but three of the fluids. This gives support to the treatment of the critical pressure S_1 as analogous or equivalent to the equilibrium spreading pressure. This will be discussed again in another connection. Applying to the silicone-water interface the well-known relation for the work of adhesion between two liquids A and B,

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}, \qquad (7)$$

it is found that the value of W_{AB} for the polymethylsiloxanes ranged from 47 to 53 ergs/cm^2, the higher values being obtained for greater molecular weights. This is only 10 to 15 percent higher than the value for non-polar hydrocarbons.

THE FORCE-AREA RELATIONS FOR POLYMETHYLSILOXANES

It was found possible to study monolayers spread on water of all but the lowest members of the series of polymethylsiloxanes of Table II. It was not possible to purify the hexamer, heptamer and octamer by percolation through Florisil because not enough was available. The silicone film was prepared by placing on the clean water surface of the film balance the requisite quantity of the compound (usually 0.04 mg) dissolved in C.P. benzene using a Harkins pipette.* The accuracy of the film balance was checked often by measuring the equilibrium spreading pressure of benzene. This was found to be 9.5 dynes/cm in agreement with Washburn and Keim.†

In Figure 1 will be found the force-area curves for a series of DC 500 fluids on distilled water at 20° C. The abscissae are expressed in square meters of surface covered per milligram of compound. The limiting areas of the film expressed in such units would be expected to be slightly different for silicones of different viscosities because of the differences in densities, since the same weight of each was used to form the films. No evidence of hysteresis was encountered provided the films were not compressed beyond 12 dynes/cm. Even when the films were compressed as much as 30 dynes/cm there was only a very slight decrease in the limiting area on decompression, and the inflection points on the curves occurred at about the same areas. The similarity of these curves and the close proximity of the points of inflection give good evidence of the structural similarity of the DC 500 fluids. This result is in full accord with the conclusions of a number of investigators‡ that the F-A curves of linear polymers are essentially determined by the properties of the monomer.

When the DC 500 fluids were allowed to remain spread on distilled water for long periods, a gradual change occurred in the properties of the film. The results of the effect of such aging are shown in Figure 2. After 24 hours of contact with the water the horizontal portion of the F-A curve disappeared. This corresponds to the disappearance of the critical pressure S_1. The same results were obtained by using either well-waxed troughs of pyrex or stainless steel and by using water which had been triply distilled in an all-tin still. The gradual disappearance of the horizontal region of the curve, the steady increase in the limiting area, and the increased pressure at very low areas all need explanation. These and

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* Harkins, W. D., and Feldman, A., J. Am. Chem. Soc. 44, 2665 (1922).

† Washburn, E. R., and Keim, C. P., J. Am. Chem. Soc. 62, 1747 (1940).

‡ Crisp, D. J., J. Colloid Science 1, 49 and 161 (1946).

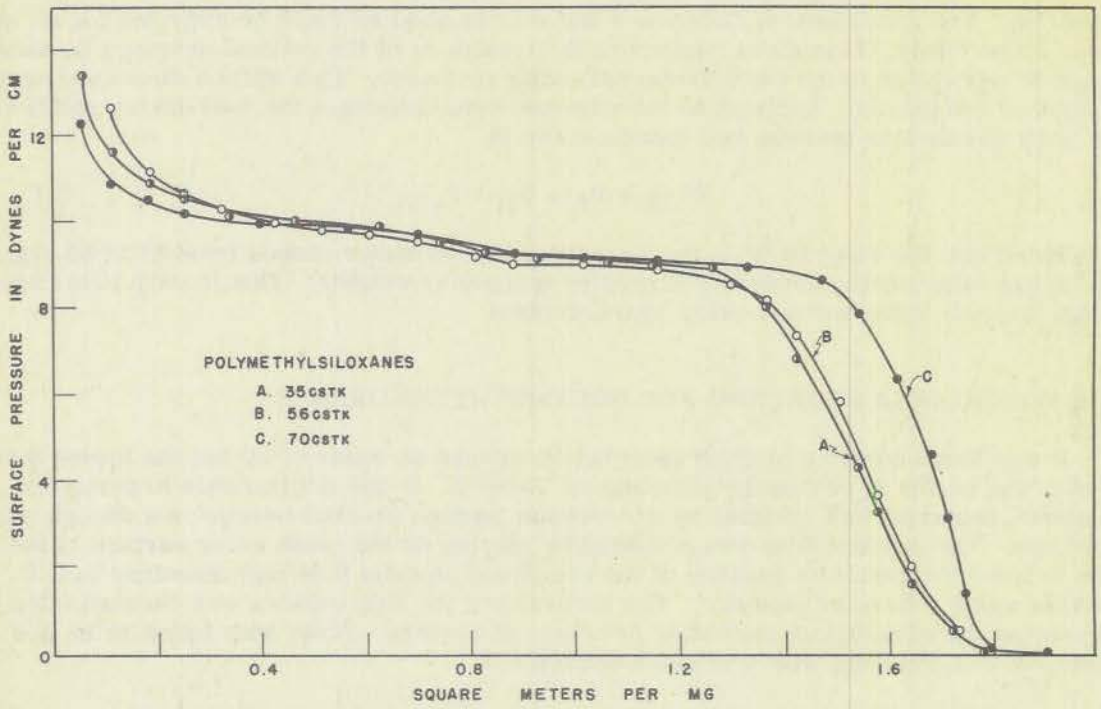

Fig. 1 - The F-A Curves for Some DC 500 Fluids

related effects caused by varying the pH and the aqueous ions present were investigated and will be reported in Part II. For the present it is sufficient to point out that the effect of aging the film on water is not significant in the length of time involved in obtaining the F-A curves reported here.

A few F-A curves were also made at 5°, 18° and 38° C to determine the effect of temperature (Figure 3). The rise in temperature caused the extrapolated area at zero pressure to increase, the region of high compressibility occurred at progressively lower pressures, and the extent of the collapse of the film at pressure S_1 increased. The spreading pressure S_1 decreases linearly as the temperature increases in agreement with the conclusion of Cary and Rideal* from their work on liquid fatty acids and esters. The discontinuity of "kink" in the flat portion of the F-A curve also occurred at larger values of the area when the temperature was raised.

Fisher-Hirshfelder atom models of the polymethylsiloxanes were made using silicon atom models which were constructed assuming: (a) tetrahedral symmetry in the valence angles, (b) a valence bond radius of 1.17 Å,† and (c) the usual calculated atom diameter of 0.8 of the sum of 1.6 Å plus twice the covalent bond radius. Inspection of the molecular model offered explanations for many of the peculiarities of the F-A curves. Each of the polymethylsiloxanes can be arranged in a caterpillar-like configuration with all of the silicon atoms in line in the same plane and all of the hydrocarbon groups on one side of

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* Rideal, E. K., An Introduction to Surface Chemistry, 2nd Ed., 129, Cambridge Uni. Press (1930).

† Pauling, L., Nature of the Chemical Bond, 155, Cornell Uni. Press (1939).

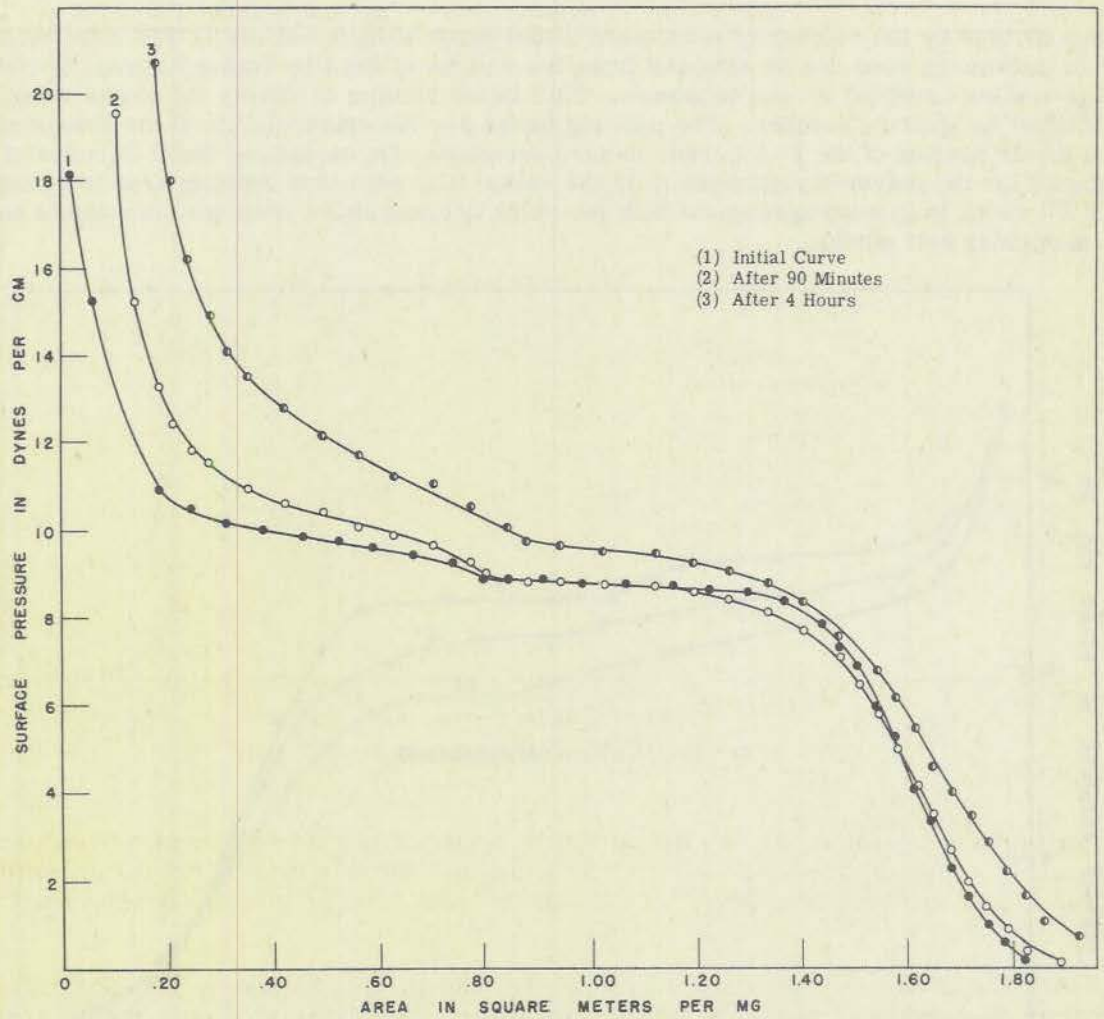

Fig. 2 - The F-A Curves for a DC 500 Fluid (56 cstk)

that plane. Such a molecule can adsorb so that all the silicon (and oxygen) atoms are in the water surface at low film pressures. Hurd* measured the molar volumes at 20° C of the polymethylsiloxanes and obtained a value of 75.5 ±0.2 ml per gram molecular weight of monomer. The contribution of the end groups may be disregarded for the higher molecular-weight polymers used here. On the basis of Hurd's measurements, the volume occupied by a single monomer is 125 Å³. Measurements on the caterpillar-like atom model showed that each monomer occupied a parallelepiped having a volume of 132 Å³, a height of 5.6 Å and an area of 22.7 Å². This value of the volume per monomer is in reasonable agreement with Hurd's considering the fact that adjacent molecules can insinuate themselves a small distance inside the outer boundaries of the parallelepiped.

The abcissae of the F-A curves for the DC 500 fluids can now be expressed in square Ångstroms per monomer, for the area per monomer is the area covered by the film on the

* Hurd, C. B., J. Am. Chem. Soc. 68, 364 (1946).

trough divided by the number of monomers in the mass of material used. The total number of monomers used can be obtained from the volume of the film (mass/density) divided by the volume occupied by one monomer. This latter volume is simply the molar volume divided by Avogadro's number. The limiting areas are the extrapolation of the low-pressure linear portion of the F-A curves to zero pressure. On examining the F-A curve of Figure 8 for the polymethylsiloxane fluid (35 cstks) it is seen that limiting area is actually 22.9 $Å^2$ which is in good agreement with the value derived above from measurements on the molecular ball model.

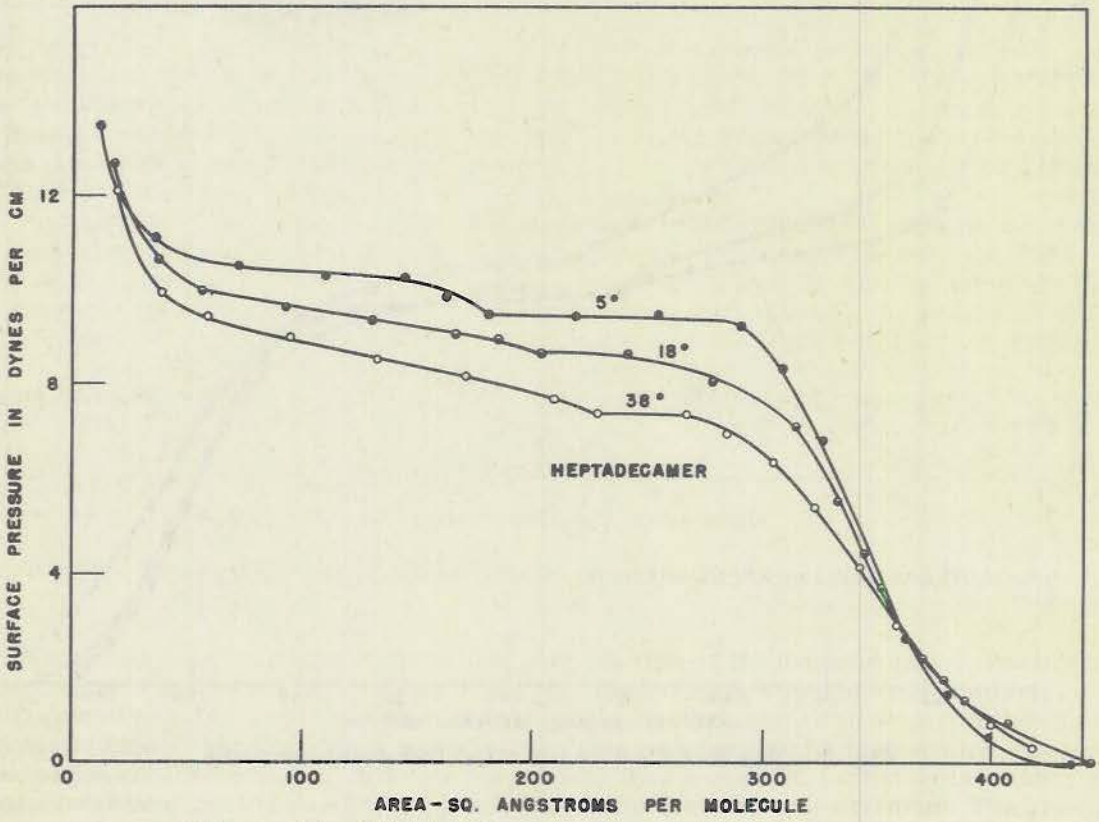

Fig. 3 - The Effect of Temperature on the F-A Curve of the Linear Polymethylsiloxane Heptadecamer

The changes in the molecular packing and orientation involved in compressing a polymethylsiloxane film can now be outlined. The close-packed phase with every oxygen and silicon atom still adsorbed at the surface appears at pressures of less than 1 dyne/cm. This phase has a moderate compressibility which is a measure of the ease with which some of the oxygen and silicon atoms can be squeezed out of the surface. If no large segments of molecules are pushed out of the monolayers, a change in the arrangement of the atoms takes place which ends at an area of approximately 16 $Å^2$ per monomer. In this state of compression the average thickness of the film is computed to be 7.9 Å, but no disposition of the atoms with all the silicons lying in the surface will produce a thickness of 7.9 Å. However, a regular "zig-zag" arrangement of the atoms of the molecule is possible for which the area occupied by each monomer is only slightly smaller than in the flat caterpillar configuration,

and the height of the molecule is then approximately 7.9 Å. The new configuration is such that only every other silicon (or oxygen) atom is adsorbed at the air-water interface. In that configuration the molecule is much more flexible and can be considerably twisted and bent without strain. This may explain what goes on in the region of high compressibility beginning at 16 Å per monomer. Here the molecules can coil or fold up more easily and portions can eventually be pushed out of the interface. The flatness of the graph in this region indicates the occurrence of some important molecular transformation. It was considered possible that the siloxane chain was being coiled up to form a helix whose axis was parallel to the surface of the water.

The film appeared to be liquid at all stages. It is noteworthy that even when the films were subjected to pressures as high as 45 dynes/cm no collapse of the film was observed. At the average thickness of 70 Å the film became relatively imcompressible and the bulk properties of the liquid emerged. In fact, careful inspection of the film showed striations due to varying thicknesses in different portions of the film. In the highly compressible region there is a small change in the slope of the curve which disappears after a small rise in pressure. This occurred with each DC 500 fluid tried at about 0.80 square meters/mg, which corresponds to about 10.0 $Å^2$ per monomer and a film thickness of 12.5 Å. This discontinuity occurred in every F-A curve whether stainless steel or pyrex troughs were used and also with two different torsion heads.

The experiments on films of the pure polymethylsiloxanes were guided by the preceding conclusions. In Figure 4 are given the F-A curves at 20° C of the heptadecamer and nonamer, while those of the dodecamer and octamer are in Figure 5. It was possible to express the abscissae in terms of more useful units (square Angstroms per molecule) because the molecular weights of those compounds were known. The curve for the heptadecamer resembles closely those of the higher molecular weight polymethylsiloxane mixtures shown in Figure 1. An important difference was that the heptadecamer film became rigid at about 12.5 dynes/cm. On further compression the film crumpled, and it did not spread again on decompression. The lack of reversibility of the highly compressed film may be due to a chemical reaction with material in the water, and it will be discussed again in Part II.

The points of inflection have been indicated by letters on the curve for the heptadecamer (Figure 4). At specific areas larger than that indicated by point A, the film is apparently gaseous. Around pressures corresponding to point A the film is a close-packed monolayer with every silicon and oxygen atom in the surface of the water since the limiting area agrees closely with that calculated from the caterpillar ball model. Extrapolating the linear portion of the curve near point A to zero pressure results in an area of 395 $Å^2$ per molecule which corresponds to an average film thickness of 5.9 Å. This is to be compared with the area of 415 $Å^2$ per molecule and the thickness of 5.6 Å measured on the caterpillar ball model. It is not surprising that the measured specific area is smaller than the calculated since the latter corresponds to the area of the enveloping parallelepiped. Point B corresponds to a thickness of the monolayer of 7.9 Å which, as shown earlier with the ball model, corresponds to a "zig-zag" configuration with every other oxygen (or silicon) atom out of the surface of the water. The change in slope at point C occurs at an area per molecule of 175 $Å^2$ corresponding to a film thickness of 12.7 Å. Now a horizontal helical ball model coiled into turns containing 6 monomer units each has a height of 12.5 Å. It was not possible by manipulating the ball model to wind it into a close-wound helix having a smaller diameter. Point D marks the location where the area per molecule (40 $Å^2$) approximately equalled the cross-sectional area of the straight caterpillar molecule taken at right angles to its long axis.

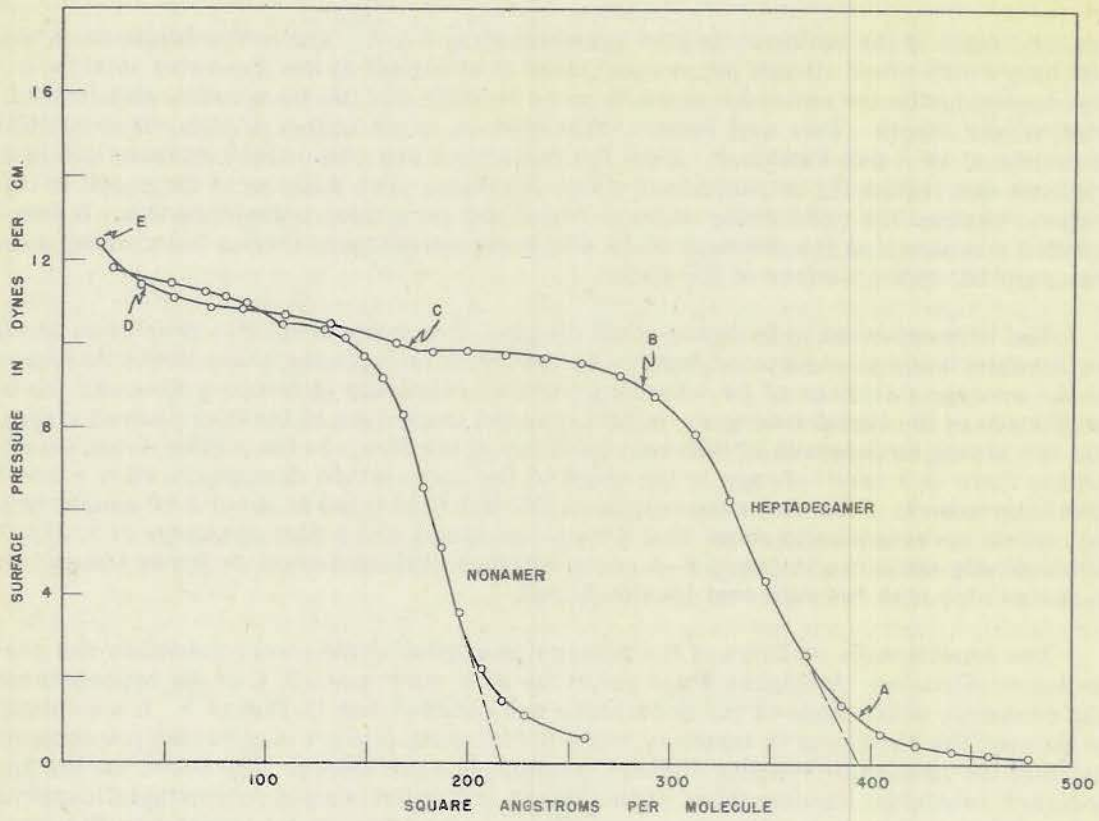

Fig. 4 - The F-A Curves of the Polymethylsiloxane Heptadecamer and Nonamer

From this interpretation of the behavior of the film of the heptadecamer, it would be expected that the nearest homologues of shorter chain length would behave similarly, but the similarity should eventually disappear when the number of silicon atoms in the chain become too few to permit coiling into a helix. This was found to be true and the octamer was the lowest homologue to show any similarity. The region BC varied as the chain length decreased until it was no longer evident in the curve for the octamer. The area for the dodecamer and nonamer molecules (state A) were found with the data of Figures 4 and 5 to be 270 $Å^2$ and 216 $Å^2$ respectively, while the corresponding heights were 6.06 Å and 5.6 Å. These are to be compared with areas of 294 $Å^2$ and 221 $Å^2$ and a height of 5.6 $Å^2$ calculated from the straight caterpillar ball models. From these graphs the heights found for the coiled helical molecule (corresponding to state C) are 13.1 Å and 12.5 Å respectively. The pressure at which the film became solid (state E) decreased with the chain length. Thus the films of the heptadecamer, dodecamer, nonamer and octamer became solid at 12.5, 12, 11.8 and 11.5 dynes/cm. The heptamer and hexamer became solid at a pressure of somewhat less than 1 dynes/cm, and hence F-A curves cannot be given for them. These solid films did not revert to liquid films when the pressure was decreased.

The following conclusions can now be made relative to the behavior of films of the polymethylsiloxane nonamer, dodecamer, heptadecamer, or intermediate or higher homologues, or mixtures of them. At the lowest pressures the gaseous film can be compressed to a close-packed monolayer of linear caterpillar-like molecules with every oxygen (or

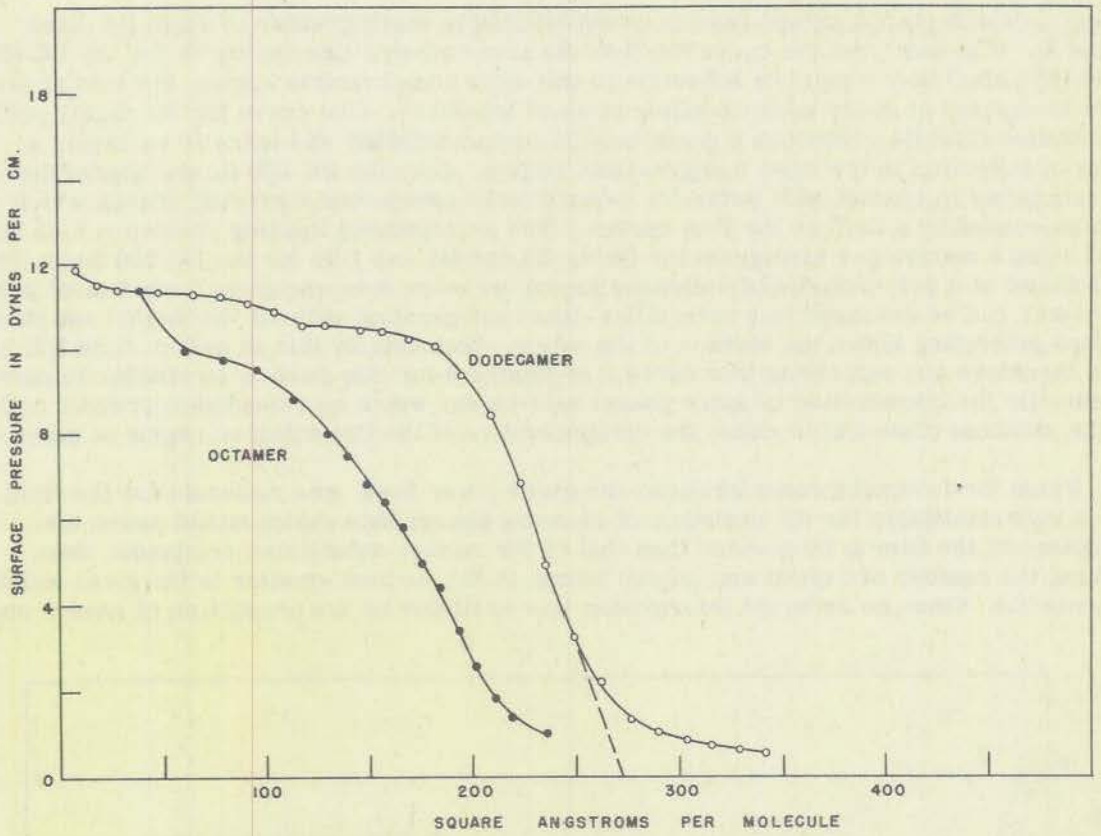

Fig. 5 - The F-A Curves for the Polymethylsiloxane Dodecamer and Octamer

silicon) atom adsorbed in the water surface (state A). On further compression the molecules buckle until every other atom of the siloxane chain is out of the surface (state B). In this state the molecules are flexible stretched-out helices and are easily compressed until they assume a close-packed helical configuration (state C). In going from state C to state D the axes of the helices are tilted out of the surface and the helices are gradually uncoiled by the pressure until the film is squeezed into an arrangement of nearly close-packed rods (state D) which are oriented so as to present their ends to the water surface rather than their lengths. In this state van der Waals forces can come into action to permit the monolayer to become solid at higher pressures (state E). Mixed polymethylsiloxanes like the more viscous DC 500 fluids do not freeze at high pressure because of the wide distribution of chain lengths.

THE FORCE-AREA RELATIONS FOR POLYMETHYLPHENYLSILOXANES

The area coordinate in the F-A curves for the polymethylphenylsiloxane fluids was expressed in square meters per milligram due to the unavailability of information on the molecular weights and molar volumes. The F-A graphs are similar in shape to those of the polymethylsiloxanes, the difference becoming more prominent with increase in aromaticity. In Figure 6 will be found the graphs for fluids B3 and B4, both of which have viscosities of 50 cstks, and the graph of DC 500 fluid (35 cstks) for comparison. The

extent to which phenyl groups have been substituted is much greater in fluid B4 (see Table I). It is seen that the curve for fluid B3 is very much like the curve for the DC 500 fluid (35 cstks) with a point of inflection in the most compressible region, but less pressure is exerted at every corresponding point of the curve. The curve for the highly phenyl substituted fluid B4 evidences a great loss of compressibility and there is no longer a point of inflection in the most compressible region. Like the DC 500 fluids, these films on remaining in contact with water for many hours experienced a gradual change which was evidenced by a drift in the F-A curves. The extrapolated limiting areas are 1.45 and 0.95 square meters per milligram for fluids B3 and B4 and 1.95 for the DC 500 fluid. The ball model of a polymethylphenylsiloxane having no more than one phenyl substituent per monomer can be arranged in a caterpillar-like configuration with all the methyl and phenyl groups projecting above the surface of the water. Undoubtedly this is true of fluid B3, and it is therefore not surprising that curve 2 of Figure 6 for this fluid is so similar to curve 1. Eventually the introduction of more phenyl side chains would be expected to prevent coiling of the siloxane chain and to cause the disappearance of the flat collapse region of curve 1.

From the foregoing considerations the much lower area per molecule for the fluid B4 is understandable for the presence of so many phenyl side chains would cause the thickness of the film to be greater than that of the methyl-substituted compound, thus making the number of oxygen and silicon atoms in the surface smaller in the given weight of material. Since no accurate information was available on the proportion of phenyl and

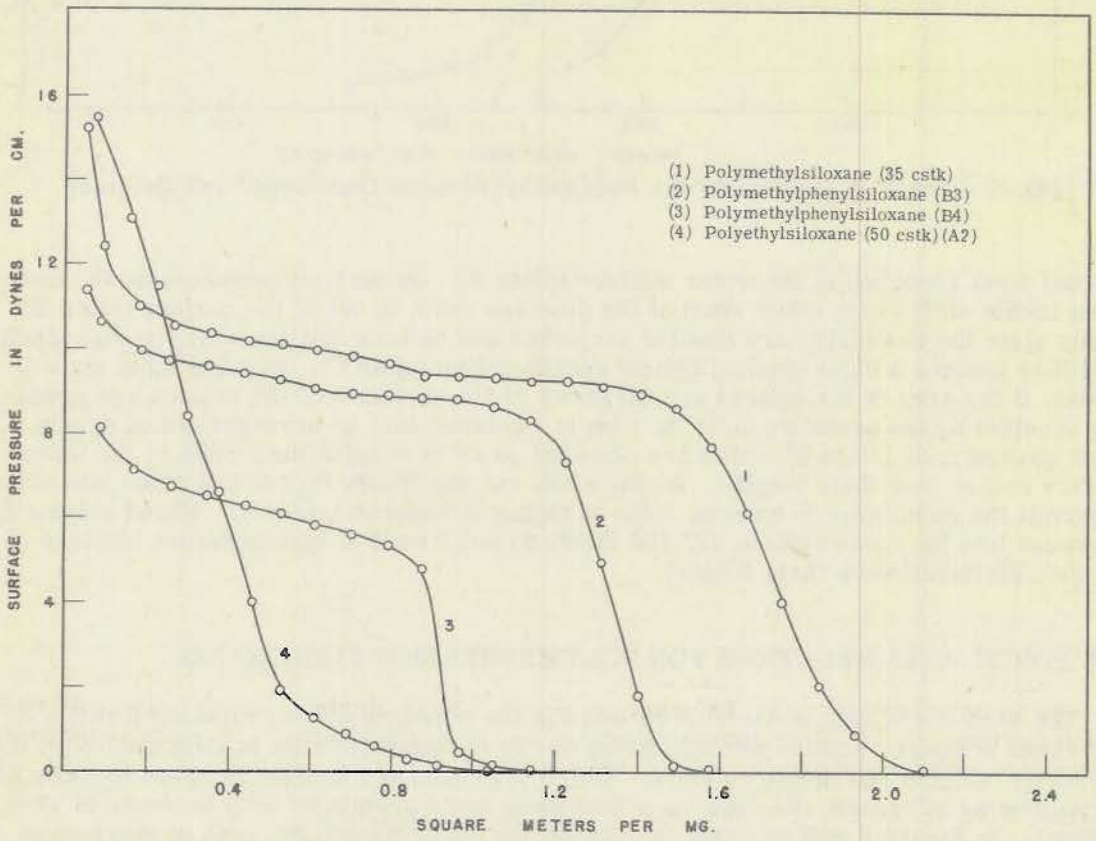

Fig. 6 - The F-A Curves for Different Types of Linear Polyorganosiloxanes

methyl groups in these polymers, a comparison based on the ball models could not be made of the area occupied by each monomer.

THE FORCE-AREA RELATIONS FOR POLYETHYLSILOXANES

The F-A curve obtained with the polyethylsiloxane fluid A2 (50 cstks) is given in Figure 6 (curve 4) and again in Figure 9. Due to the lack of information on either the molar volume or the molecular weight, it was only possible to express the areas in square meters per milligram. Like the other polyorganoxiloxanes already described, the F-A curves were reversible but did slowly change as the film aged while spread out on the water. It will be noted that the F-A curve 4 of Figure 6 is very different from the others. It is similar to the curves obtained by Harkins, Carman and Ries* from polymers of ω-hydroxydecanoic acid which were shown to lie flat on the water surface at low pressures. The polyethylsiloxane films did not collapse at high pressures but became thicker and more viscous until at pressures of 17-18 dynes/cm striations appeared. At the highest pressures attained ($18\frac{1}{2}$ dynes/cm) the films were liquid and viscous.

The ball model of a polyethylsiloxane was impossible to arrange in the caterpillar-like configuration described earlier. This is because of hindrance to the rotation of the ethyl side chains about the silicon-to-carbon bond. However, the ball model could be arranged in configurations such that some but not all of the silicon and oxygen atoms could emerge from the surrounding sheath of ethyl groups to contact the surface of the water. Therefore, only an occasional silicon or oxygen atom of the polyethylsiloxane molecule is able to absorb at the water-air interface, and it would be expected to behave much more like the ω-hydroxydecanoic acid polymers than the other silicones described here. The limiting area per polyethylsiloxane monomer is not known, due to the lack of molecular-weight data. It is very likely that the compressed films are formed by a random buckling and folding of the monolayers to create a thick film like the "overfilm" of polyacrylates described recently by Crisp.†

POTENTIAL-AREA RELATIONS

The Volta potential difference, ΔV, due to the presence of each silicone film on the distilled water of the film balance is expressed as a function of the degree of packing in Figures 7, 8 and 9. The corresponding F-A curves are given for comparison. The ordinate of the curve marked μ_n is the normal component of the dipole moment for that degree of packing, and it is calculated as usual by

$$4\pi N\mu_n = \frac{\Delta V}{300} \qquad (8)$$

where N is the number of molecules per unit area. Due to limitations set by the units used in plotting the abscissae in each figure, the ordinate μ_n in Figure 7 was given in Debye units per molecule, in Figure 8 it was in Debye units per monomer, and in Figure 9 it was expressed in arbitrary units which are equivalent to Debye units per monomer multiplied by an unknown constant. The curve of Figure 9 was obtained by multiplying ΔV by each corresponding value of the abscissa A in square meters per mg. For each substance studied

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* Harkins, W. D., Carman, E. F., and Ries, H. E., J. Chem. Phys. 3, 692 (1935).

† Crisp, D. J., J. Colloid Science 1, 49 and 161 (1946).

on distilled water, the ΔV -A and μ_n -A curves were reproducible and free from hysteresis.

As would be expected, the F-A and μ_n -A curves are similar for the heptadecamer and the DC 500 fluid, both revealing that μ_n is zero for all values of A for which the molecules are not in close proximity. It rises rapidly to a maximum value as A approaches and equals the area of closest packing of the flat caterpillar-shaped molecules. As buckling of the film occurs at higher film pressures μ_n decreases nearly linearly, and it approaches zero as the greater portion of the monolayer collapses into a thick film showing striations. The previously described geometrical rearrangements which occur in the film after buckling starts do not cause changes of slope in the ΔV -A or μ_n -A curves. The maximum value of μ_n per monomer calculated from Figure 7 is 1.5/17 or 0.089 Debye units. This is to be compared with the value of 0.087 Debye units per monomer as read from the maximum of Figure 8. This is a good agreement for results obtained for a pure compound and a mixture of homologues. It is evident from the μ_n -A curve of Figure 9 that the polyethylsiloxane fluid behaves quite similarly to the polymethylsiloxane fluids. The linear drop in the μ_n -A curve after buckling commences is quite common in other types of films, and it is also assumed to be caused by disorganization of the dipoles during the formation of the "overfilm." The low-pressure electrical behavior observed is different from anything reported heretofore. One cause may be that electrical compensation in the caterpillar-shaped molecules exists unless forces arising during close packing can disturb the situation. These effects may be due to: (a) bond strains, (b) induction effects between molecules, or (c) compensating effects due to the orientation of adsorbed molecules of water which may disappear during close packing and buckling as the silicon and oxygen atoms are lifted out of the water. Further

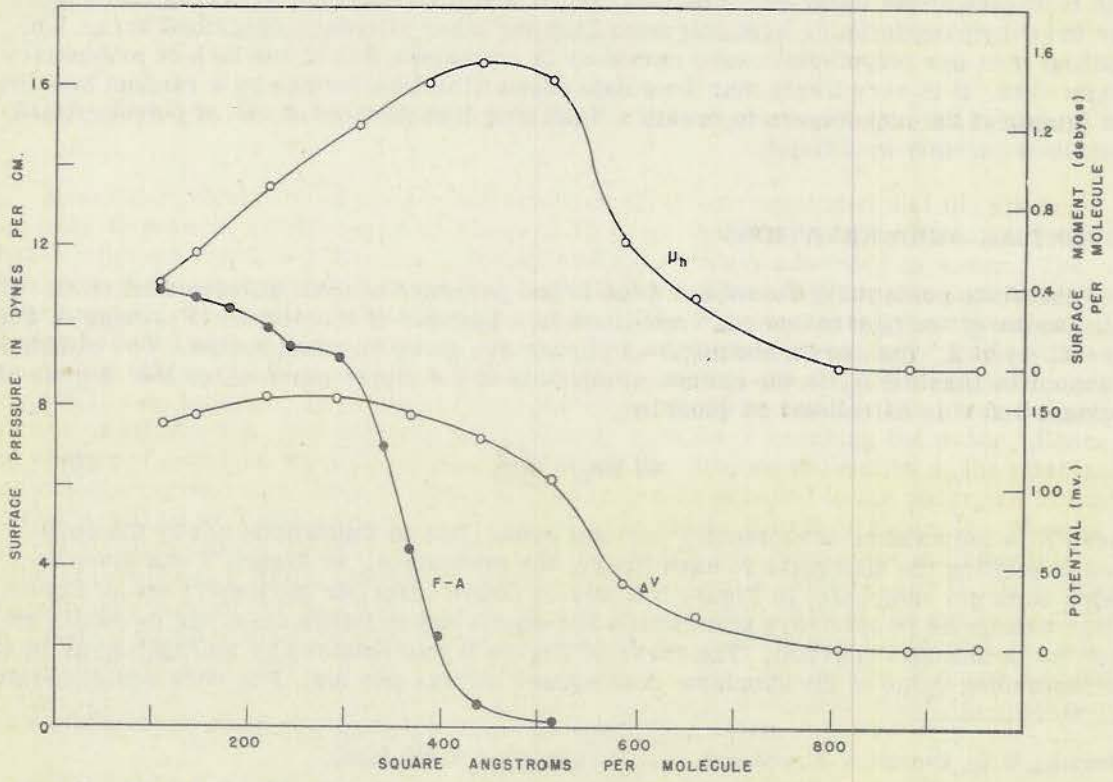

Fig. 7 - The F-A, ΔV -A, and μ_n -A Curves for the Polymethylsiloxane Heptadecamer

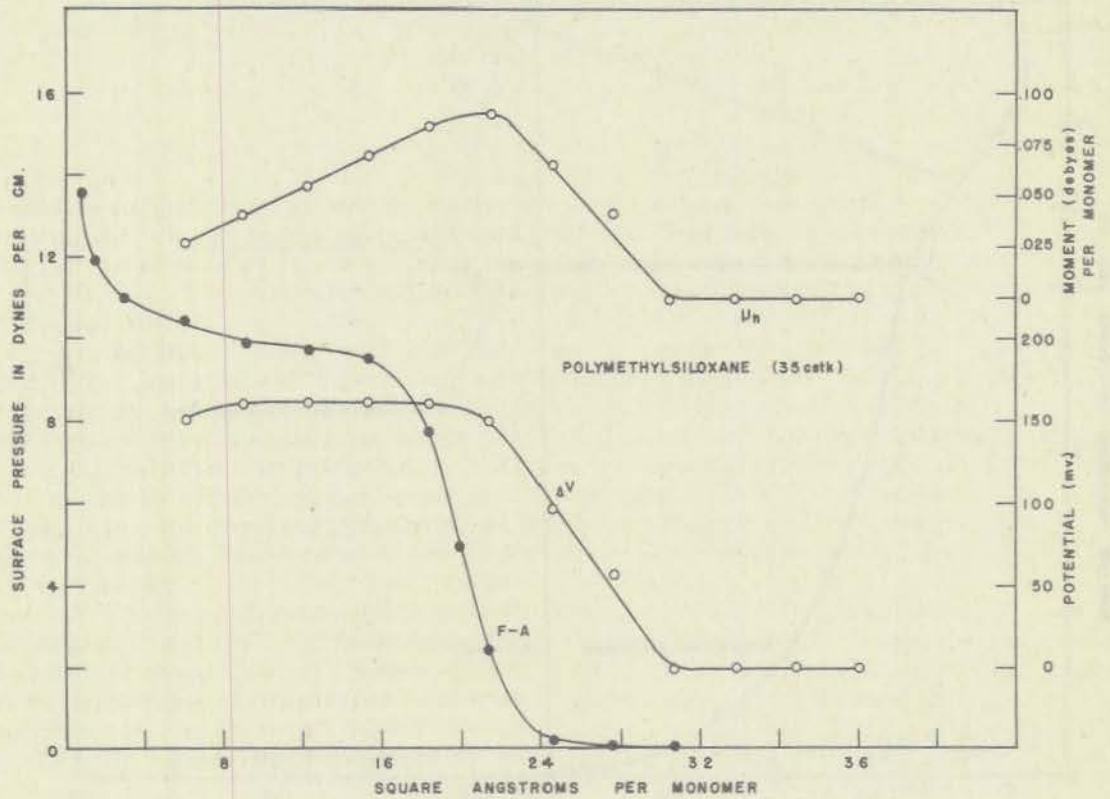

Fig. 8 - The F-A, ΔV -A, μ_n-A Curves for a DC 500 Fluid (35 cstk)

discussion of these electrical properties and their relation to structure will be given in Part II.

DISCUSSION

The collapse phenomena found in studying the F-A relations in the silicone monolayer explain some of the effects described earlier in connection with the search for the equilibrium spreading pressure. In no instance could a drop of any silicone fluid exist on water in equilibrium with the silicone monolayer. The remarkable phase transition discovered in monolayers of the higher molecular-weight polymethylsiloxanes (see state C in Figure 4) is responsible for the "critical spreading pressure." The conditions of the polymethylsiloxane molecules in the adsorbed film at high pressures (states D and E in Figure 4) and at very low pressures (state A) are apparently not found in the bulk liquid. However, the coiling of the molecule encountered in states B and C is believed to be characteristic of the configuration of the molecules in the 3-dimensional liquid state. As evidence it should be noted that the "critical spreading pressure" S_1 has been shown to be approximately equal to the spreading coefficient S_{AB} which is calculated from the surface and interfacial tensions. Also it has been shown that S_1, like the equilibrium spreading pressure of many of these liquids, decreases linearly as the temperature rises. The logarithmic decrease in S_1 as the viscosity rises is also indicative.

containing 6 monomers per turn is remarkable as a phenomenon of surface chemistry. It also can help explain some of the properties of the silicones in the 3-dimensional state. The observed shift with temperature of the "kink point" C of Figure 4 as shown in Figure 3 means that each horizontally oriented helical molecule lengthens considerably as the temperature rises. An order of magnitude calculation can be made of the thermal expansion of the helix by assuming that the temperature change of the radius can be neglected and that the projected area of the horizontal helix as it lies on the water is equal to that of a rectangle of area S with length L equal to the length of the helix and a width equal to the diameter of the helix. A simple calculation shows that $(1/S)(dS/dT) = (1/L)(dL/dT)$. From Figure 3 it was calculated that at 5° C, S was 6.7 Å² per monomer while at 20° C it was 9.4 Å². Hence $(1/S)(dS/dT) = 0.0075$ per degree centigrade. The coefficient of linear expansion of such a fluid is approximately 0.3×10^{-3} per degree centigrade. Hence $(1/L)(dL/dT)$, the linear coefficient of thermal expansion of the helix along its axis is approximately 25 times the linear coefficient of expansion of the bulk liquid.

It is suggested that the remarkably high viscosity indices of the methyl-substituted silicones (or the low temperature coefficients of viscosity) are caused by the opposing actions of two molecular mechanisms: (a) the effect of increased temperature in separating the molecules causing the viscosity to decrease; (b) the effect of increasing temperature in lengthening the helically coiled polymers causing the viscosity to increase. Effect (a) is common to all liquids while effect (b) is more evident in long-chain molecules, being most pronounced in the linear polymers so bonded and free from steric hindrances as to be most able to coil. Of the polyorganosiloxanes studied, the polymethylsiloxanes have just been shown to have the most pronounced ability to coil. The low-aromaticity polymethylphenylsiloxanes were next, with increase in the aromaticity operating to hinder coiling. Finally the polyethylsiloxanes exhibited the least ability to coil. This relative order agrees with the order of decreasing viscosity indices. Hence it is concluded that the high viscosity indices of the silicones are due to the tendency of the siloxane chain to coil into a helix, and this property is most evident in the methyl-substituted compounds because they are the most compact hydrocarbon side chains and cause the least steric hindrance to the coiling of the chain.

The conclusion that the helical coil contains six silicon atoms (or six monomers) is given support by recent work of Wilcock* who estimated from the Kausmann-Eyring theory of the activation energy for viscous flow that the flow units involved in the linear polymethylsiloxanes consisted of 6 to 7 silicon atoms, the former value being preferred. The flexibility of the polyorganosiloxane chains may be increased even more than is evident in the studying Fisher-Hirschfelder ball models if the silicon-carbon bond angle is as variable as has been suggested by the x-ray work of Roth.†

CONCLUSIONS AND RECOMMENDATIONS

The linear dimethyl-substituted silicone fluids (DC 500, DC 200) can, under certain conditions, be strongly adsorbed on water although in the bulk state they have a relatively small affinity.

Much evidence was found for concluding that in the bulk state the molecules comprising these fluids are coiled into helices which expand along their axes when heated. This

* Wilcock, D. F., J. Am. Chem. Soc. 68, 691 (1946).

† Roth, W. L., J. Am. Chem. Soc. 69, 474 (1947).

phenomenon may account for the very high viscosity indices of the dimethyl silicones since such a behavior would tend to compensate for the normal decrease of viscosity with rise in temperature.

The force-area data revealed that organic substitution other than methyl tended to reduce ability to coil, thus preventing the compensating mechanism from operating. This conclusion agreed with the known smaller viscosity indices exhibited by diethyl- (DC 400) and methyl-phenyl- (DC 550, DC 700) substituted siloxanes.

The force-area curves were found to change in shape with time, pointing to a reaction with water or substances present in the water. The surface-potentials of the silicones were unusual in that the potential was zero until the molecules in the surface were compressed to a point where they occupy two-thirds of the available area.

It is recommended that this study be pursued further to elucidate the unusual potentials and especially the unusual time effect shown by the silicones on aqueous solutions.

ACKNOWLEDGMENTS

The pure linear polymethylsiloxanes were made available through the cooperation of Dr. S. Bass and Dr. M. J. Hunter of the Dow-Corning Corporation. The conclusions from infrared absorption studies used in preparing the type classifications of Table I are excerpts from a larger spectroscopic study of the silicones which were made available through the cooperation of Don C. Smith, Head of the Chemical Spectroscopy Group of this laboratory. An acknowledgment is due to Edwin M. Solomon for assistance in obtaining many of the force-area and potential-area curves.

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