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The determination of the cross-sectional area of a stearic acid molecule

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THE DETERMINATION OF THE CROSS-SECTIONAL AREA OF A STEARIC ACID MOLECULE.

by

Michael Stacey Dryer
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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

By Michael S. Dryer

Approved by Howard E. Sheffer

May 24, 1960

gift of the author, October 20, 1960

ACKNOWLEDGEMENT

Few students, in the course of their four years of college have had the opportunity to be associated with a professor with such devotion to his students. I can recall one phrase, which has become immortal to me, that might underscore this statement.

The Professor was engaged in research for one of the companies in Schenectady, and thus, a salesmen had come during a laboratory period to offer his wares. While I stood inconspicuously outside his office, I saw him look up with a stern expression, and say,

> "What are _you_ doing _here_? Today, I spend
> with my students, tomorrow I work for the
> company!"

Thus, for his immeasurable assistance during the preparation of this study, for the future rewards that might come to me through his ability to instruct in the fields of Organic Chemistry and Colloid Chemistry and for being such a good, and tolerant, friend, it is with deepest gratitude, and utmost sincerity, that I humbly dedicate this thesis to Professor Howard Sheffer.

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Introduction and History.

The fundamental relationship in determining the area per molecule is:

$$A = \frac{SM}{g/c \times v \times N}$$

where A = area per molecule.

S = area occupied by the monolayer.

M = molecular weight.

g = grams of stearic acid in volume c.

c = volume of solution.

v = aliquot of c delivered to the surface.

N = Avogadro's Number.

Each of the terms in the above equation will be discussed in detail below.

S. The Area Occupied by the Monolayer.

The apparatus used was the Cenco No. 70551 Hydrophil Balance which is a long, rectangular, shallow metal trough, the width of the trough is, of course, constant during a determination. The length occupied by the monolayer may be varied by means of the metal barrier supplied with the apparatus. The length of the trough is graduated in centimeters, the zero reading is the point at which the mica float traverses the width of the trough.

The mica float is attached to the sides of the trough by means of platinum foil, using DuPont cement. In order to ensure accurate measurement of film tension, the mica float must be allowed to swing freely. Thus, the zero point is not constant for the float position is variable. The variation, however, is small compared to the area occupied by the monolayer in these determinations.

One of the assumptions in using the equation given previously is that the fatty acid forms a monolayer completely free of solvent. Whether this assumption is valid is part of the object of the present study.

After evaporation, the layer should consist only of stearic acid. However, in a paper issued by the Division of Colloid Chemistry of the American Chemical Society, entitled "Abstracts of Papers Presented at Atlantic City, New Jersey, September 13 to 18, 1959," the author's attention was brought to article 14 by V. K. La Mer and Max L. Robbins, "The Effect of the Spreading Solvent on the Properties of Monolayers," which stated that benzene was adsorbed too strongly to be used as a spreading solvent. This argument was further supported by their paper,[1] and by an article by Mme. Ter Minassian Saraga.[2] K. J. Mysels[3] gives a simple graphic discussion of what happens to molecules of fatty acids when spread from benzene. The hydrophillic heads, or -COOH groups, will lie in the water, but benzene is pictured as occupying space between the tails of the molecules. Benzene would be more likely to be found in the monolayer than n-hexane because of the greater force of attraction of water for benzene than n-hexane due to its higher polarizability and its lower volatility. Thus, the area covered by a stearic acid monolayer spread with benzene may be larger than expected. Apparently, this was the case in the experimental results obtained by La Mer and Robbins.

Weight of Stearic Acid, Volume of Solution and Size of Aliquot.

The main object of the present study was to observe the effect of concentration, and consequently the aliquot on the cross-sectional area of a fatty acid molecule. The apparatus limits the range of weights of stearic acid that can be added to the surface to approximately 2×10^{-6} to 9×10^{-6} grams. The manner in which these weights of stearic acid may be delivered are varied as follows:

a.) Low concentration, large aliquot.

b.) High concentration, small aliquot.

With low concentrations of stearic acid, a large quantity of solvent is added to the surface of the sublayer. If the theory of La Mer and Robbins is to be accepted, there would be more chance of retention of solvent in method (a) than (b). Thus, various concentrations of fatty acid were used, with approximately equal repetition of varying methods of delivery, which are described below.

M. The Molecular Weight.

The values of areas of fatty acid molecules from 16-20 carbon atoms in length are approximately 22 - 23 $(\mathring{A})^2$. This could lead to only one conclusion; that the long-axis of the molecules must lie perpendicular to the surface of the water when the film is compressed and that it is indeed the cross-section of this axis that is being measured.

The following values are taken from Langmuir's article,[4]

Palmitic Acid	$C_{15}H_{31}COOH$	$21x10^{-16} (cm.)^2$
Stearic Acid	$C_{17}H_{35}COOH$	$22x10^{-16} (cm.)^2$
Cerotic Acid	$C_{25}H_{51}COOH$	$25x10^{-16} (cm.)^2$

It would seem that oleic acid, with 18 carbon atoms would fall into this category also. However, Langmuir theorizes that the double bond of the acid lies on the surface thus occupying more area of the monolayer. This corresponds to the values obtained, which are almost twice those of stearic acid.

Other Variables.

Thus, the monomolecular area is subject to the above variables and a few more. These include the hydrogen ion concentration, which pushes the curve to the left, making the cross-sectional area smaller, according to Langmuir.

The time allowed for evaporation of solvent, the nature of the solvent, and the temperature at which the run was made are other variables.

The limiting area is also dependent upon the method of extrapolation of the curve, particularly in the case of benzene as spreading solvent.

Early History.

The adsorption of films on liquids has been investigated since 1765, when Benjamin Franklin estimated the thickness of a layer of olive oil on water to be $25 (\overset{o}{A})^2$.

Irving Langmuir in 1917, examined surface films and came to the conclusion that these films were monomolecular. In his paper "The Constitution and Fundamental Properties of Solids and Liquids. II. Liquids.,"[4] he discussed the properties of oil films spread on water.

Through the efforts of Irving Langmuir, A. Marcelin, A. Pockels, Lord Rayleigh, and others, a film balance of the type shown in the appendix was developed. Of course, the first balances were crude, consisting only of a trough and paper strips to hold the monolayer, with no instrument for measuring the amount of tension produced by the film. Langmuir, however, developed the balance to the stage where tension of the film could be measured.

Thus, Langmuir had a method for measuring the area per molecule by depositing a known volume of solution having a known concentration of substance to be spread, on water, in a trough of the type shown in the diagram. The area may be varied by moving the metal barrier. The tension may be measured by knowing the torque produced on the wire, and measuring this force in dynes, and converting to dynes per centimeter.

Experimental Procedure.

The experimental procedure which was finally settled on, was as follows: the trough was rinsed once with distilled water, then wiped out with a clean cloth, then rinsed again, and finally filled to the brim with water, a slight meniscus showing. The barrier was then pushed from zero to the back of the instrument, thus removing surface active material remaining.

The solutions which were used varied in the following manner. The stearic acid was dried, for a full day, in vacuo, after recrystallization from spreading solvent. The stearic acid was then weighed on an analytical balance, and transferred to 100 ml. volumetric flasks. The benzene was of C.P. grade, and was redistilled over a one-degree range. The n-hexane, however, was C.P., but not redistilled.

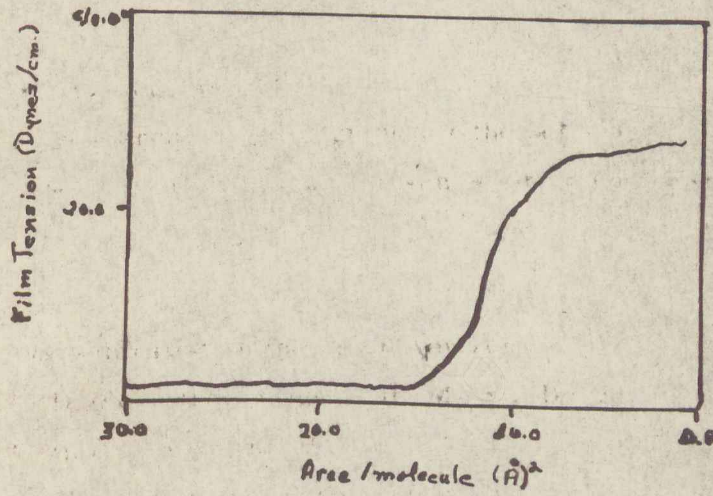
The method of delivery to the sublayer varied with the concentration. All concentrations above 0.2 gm./100 cc. were delivered by a lambda pipette. These deliveries were considered to be inaccurate due to the small volume, and the large error incurred by delivering it. The concentrations between 0.2 gm./100 cc. and 0.002 gm./100 cc. were delivered by means of the Aminco Automatic Burette. The instrument measures volumes quite accurately to plus or minus 0.0002 ml. However, this accuracy is dependent upon the observer's ability to stop the apparatus after a drop has come off the tip of the burette. However, with practice, this end is accomplished with some degree of success.

Delivery of volumes with a graduated five cc. pipette are subject to error of plus or minus 0.2 ml.

After delivery, approximately one hour was allowed for evaporation of solvent in most cases.

The metal barrier was then pushed in approximately a centimeter at a time, and the film tensions recorded.

From these considerations the area occupied per molecule of stearic acid may be determined by plotting film tension versus area per molecule, and extrapolation of the curve to zero film tension gives the area per molecule. Plots were obtained for stearic acid similar to the one below of Langmuir's.



All variables except nature of solvent and concentration of stearic acid in solvent were kept constant.

Experimental Results.

Five calibration curves were constructed approximately one month apart, and were fairly constant except for No. 1.

A full semester was spent in getting the apparatus to operate. Various types of cement were used to stick the platinum foil to the mica and to the trough. DuPont cement was found to be the best.

Threads were used instead of platinum foil and it was found that the monolayer would leak past the threads, as the threads were wetted by the water. A larger wire was inserted in the torsion part of the apparatus, but was found to have too little sensitivity to be of value in determining film tension, and the wire advised by the Central Scientific Company was used.

The tray was coated with paraffin with run 1b, and it was decided that paraffin was being dissolved by the benzene spreading solvent and thus affecting the area per molecule. The paraffin was removed after this run and the tray was coated with an Epon resin of the type, two parts Epon 1001, one part No. 3 catalyst, and cured at 350° F. for one hour.

With the exception of taking out the paraffin it was found after many repairs, that the materials offered by the Central Scientific Company should be used implicitly. Many more runs were made than are observed in the data. Due to leakage of the film past the barrier, their results are not included.

The table following on the next page gives the pertinent data.

Table of Experimental Results

Graph No.	Solvent	Conc. (gm./100 cc.)	Delivery (cc.)	Time* (min.)	Temp. (oC.)	Area/ Molecule (Å^2)	Film Tension** (Dynes/ cm.)
1b	Benzene	0.01	0.506	15	25.0	22.0	20.0
2b	Benzene	0.01	0.485	60	25.0	21.0	3.5
3b	Benzene	0.01	0.370	15	24.7	11.0	2.0
4b	Benzene	0.01	0.468	30	25.0	32.0	6.0
5b	Benzene	0.10	0.0889	60	26.4	24.0	17.0
6b	Benzene	0.01	0.512	60	23.0	26.0	26.0
7b	Benzene	0.0025	9.01	60	25.0	----	----
1h	Hexane	0.0028	1.636	20	25.0	22.0	19.0
2h	Hexane	0.0028	1.517	60	25.0	23.0	18.0
3h	Hexane	0.0011	4.10	75	23.3	25.0	25.0
4h	Hexane	0.0011	4.10	90	25.0	28.7	21.0
5h	Hexane	0.0011	4.10	***	----	24.8	11.5
6h	Hexane	0.0143	0.326	50	24.0	17.2	1.0
7h	Hexane	0.0143	0.338	90	24.0	24.2	22.5
8h	Hexane	0.2466	0.0190	60	24.0	26.3	3.0
9h	Hexane	0.2466	0.0474	60	25.0	21.8	2.5

* The time of evaporation of solvent.

** The lowest point of the straight portion of the Film Tension vs. Area/Molecule curve.

*** Overnight run.

Sample Data and Calculation.

Data from Run 9h.

Amount delivery: 0.0474 cc.

Distance of barrier: 39.0cm.

Concentration: 0.2466 gm./100cc.

Film Tension: 3.5°.

Width of Trough: 14.0 cm.

Length Weight Moment arm: 6.5 cm.

Length Film Tension Moment Arm: 7.5 cm.

Molecular Weight: 285 gm./mole

$$A = \frac{14.0 \text{ cm.} \times 39.0 \text{ cm.} \times 285 \text{ gm./mole} \times 10^{16} (\mathring{A})^{2} / \text{cm.}^{2}}{0.2466 \times 10^{-2} \text{ gm./cc.} \times 0.0474 \text{ cc.} \times 6.02 \times 10^{23} \text{ molecules/gm.-mole}} = 22.1 (\mathring{A})^{2}.$$

3.5° Film Tension is equivalent to 7.0 mg. according to calibration curve No. 5.

$$\text{F.T.} = \frac{7.0 \text{ mg.} \times 6.5 \text{ cm./}7.5 \text{ cm.} \times 10^{-3} \text{ gm./mg.} \times 980 \text{ cm./sec.}^{2}}{14.0 \text{ cm.}} = 0.424 \frac{\text{dynes}}{\text{cm.}}$$

Discussion.

As may be seen from runs 1h-9h, the average cross-sectional area of a stearic acid molecule with hexane as solvent is 23.7 $(\mathring{A})^2$. This value varies a small degree from X-ray diffraction studies, which gives a cross-sectional area of 22.4 $(\mathring{A})^2$.

It is the author's opinion that hexane should be used as solvent rather than benzene. For instance, run 1b, (with benzene as solvent), shows two breaks in the curve and it is questionable which break should be extrapolated. Runs 2b, 3b and 4b show very low film tensions and do not allow much room for extrapolation. In runs 5b and 6b, the curve rises sharply immediately from zero film tension. Run 7b is meaningless.

With the exception of runs 6h and 8h, the hexane runs were invariably successful. 6h gives a small curve for extrapolation and curve 8h gives two possible extrapolation points.

Whether benzene is irrevocably contained in the monolayer, has not been borne out in these experiments. However, it does seem that n-hexane is the more desirable solvent.

If the one run with the lambda pipette and one of the three runs with the 5cc. pipette that does not agree with the other two are not included, the data show six values between 21.8 and 25.0 $(\mathring{A})^2$. A plot of these six points indicates a trend toward higher cross-sectional area with larger aliquots.

It must be remembered, that if the theory of La Mer and Robbins is correct, that indeed the more solvent, the more chance for its retention in the monolayer. Thus, the graph at the end of this paper shows the general trend of the results. More work needs to be done to confirm this.

The study of monolayers is useful in obtaining a true understanding of what molecules really are. We know they exist, but there are few opportunities to see that they are acutually there, physically.

With the advent of X-ray diffraction, Langmuir's wet method is subject to too many variables to be useful in measuring the cross-sectional area of a molecule. That a monolayer does exist, and that the concentration of fatty acid in solvent does play a role in such a determination may be concluded from the above.

Conclusions.

Three conclusions have been observed at the completion of this study:

1.) The determination of cross-sectional area is best done without paraffin in the trough.

2.) n-Hexane is a more desirable solvent than benzene.

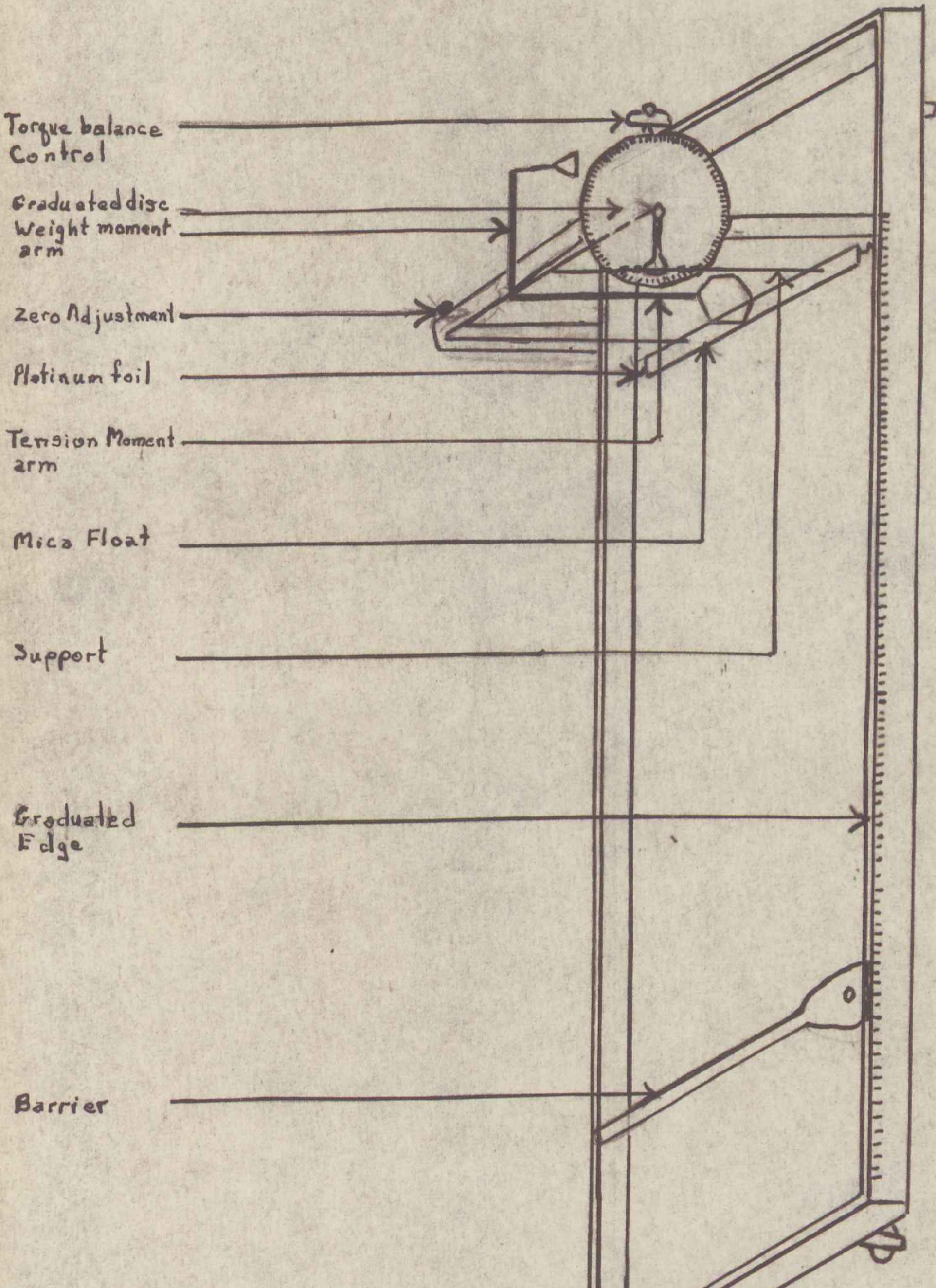
3.) The weight of fatty acid per 100cc. solvent should be from 10^{-2} to 10^{-3} grams and the automatic burette should be used to deliver these concentrations.

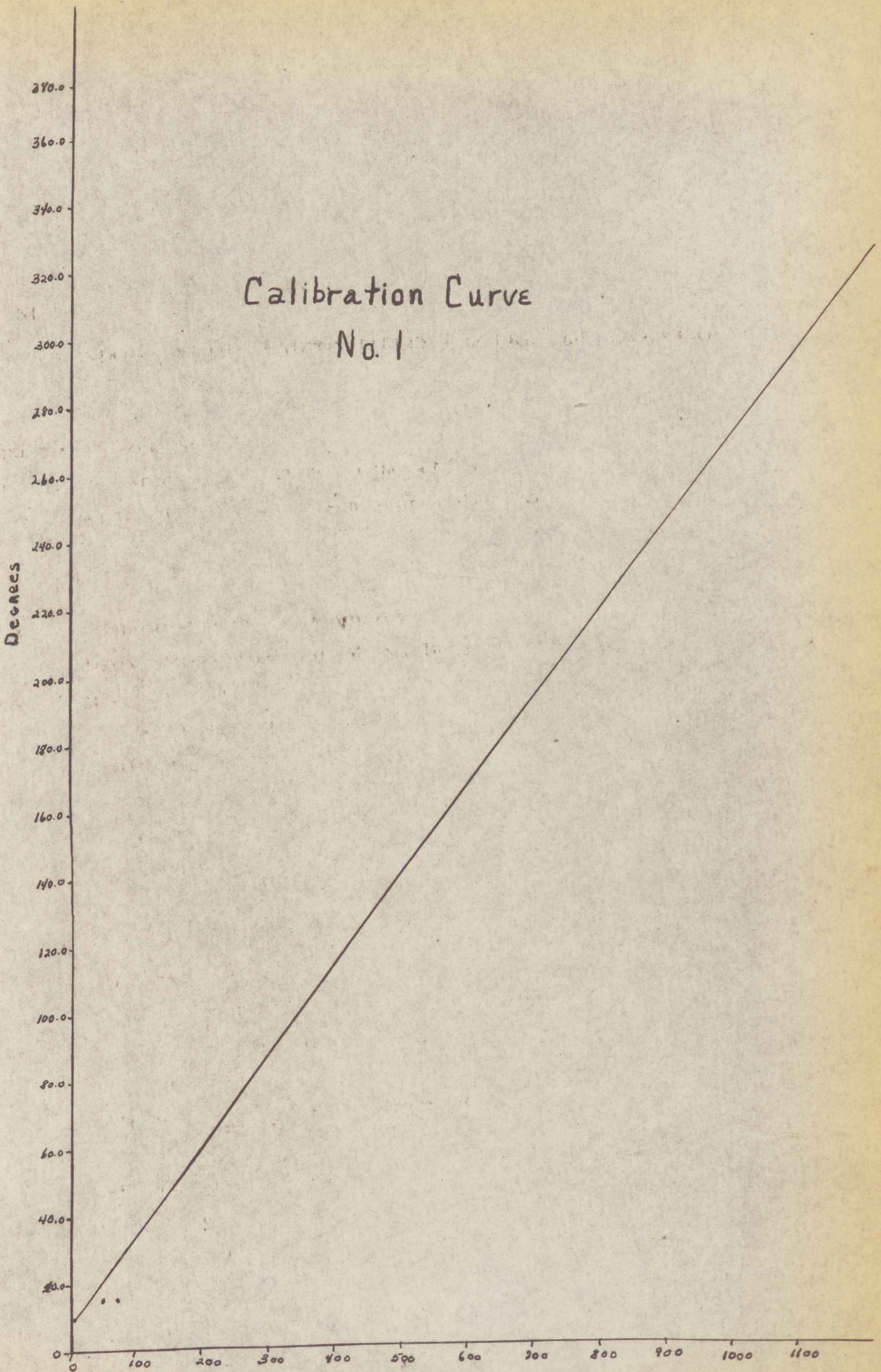
References.

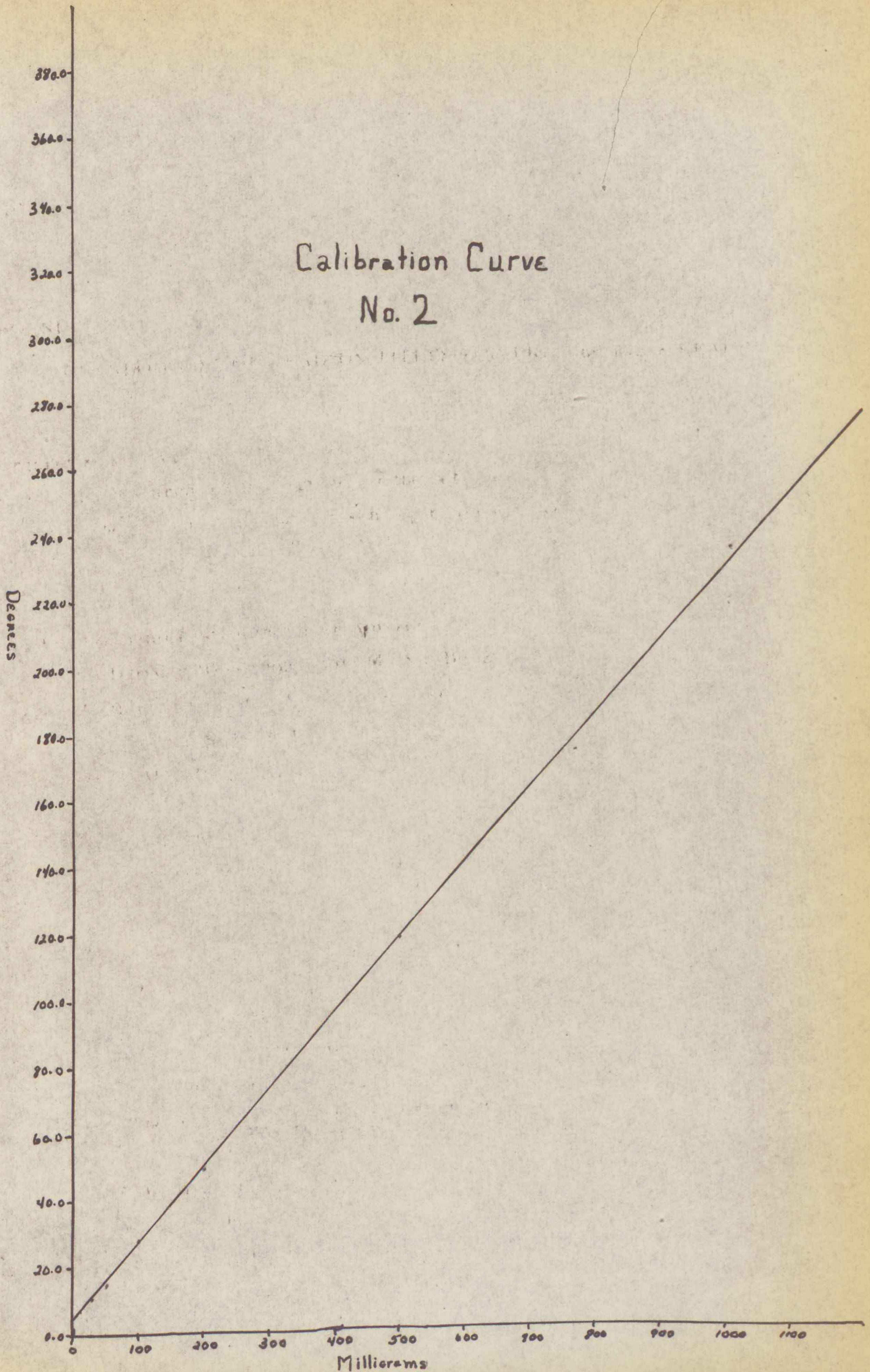
1. "Properties of Monolayers," V.K. La Mer and Max L. Robbins, Journal of Physical Chemistry, 62, pp. 1291-1294, (1958).
2. Mme. Ter Minassian-Saraga (no reference to her paper), Journal of Physical Chemistry, 62, pp. 1294-5, (1958).
3. Introduction to Colloid Chemistry, K. J. Mysels, Interscience Publishers, Inc., (New York, 1959) pp. 180-182.
4. "Fundamental Properties of Solids and Liquids. II. Liquids," I. Langmuir, Journal of the American Chemical Society, 39, pp. 1848-1906, (1917).
5. Organic Colloids, Bruno Jirgensons, Elsevier Publishing Co., (New York, 1958) pp. 79-85.
6. Colloid Chemistry, J. Alexander, Reinhold Publishing Co., V, (New York, 1944) pp. 22-102.

APPENDIX

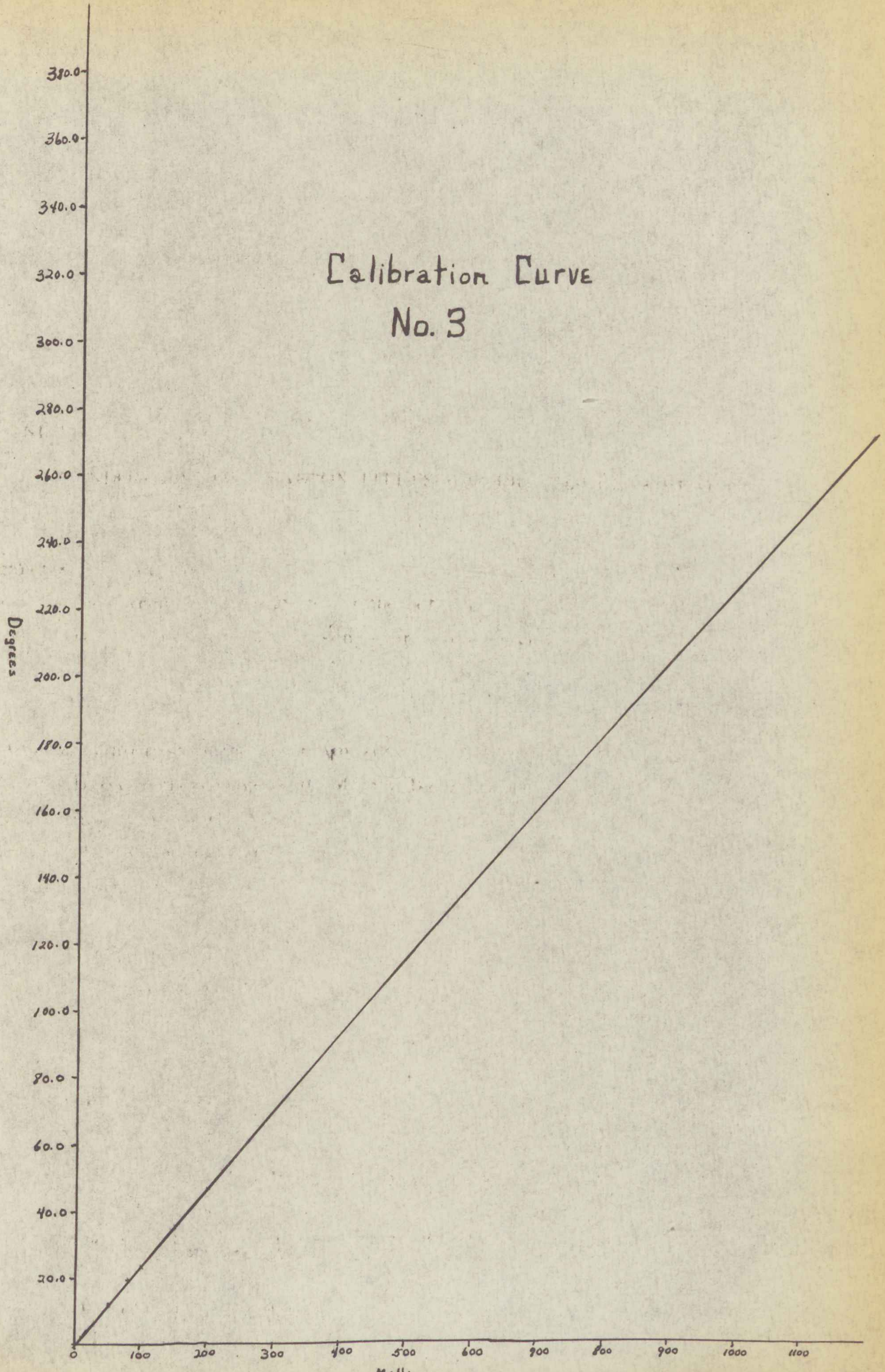
Diagram of Catalogue No. 70551 Cenco Hydrophil Balance



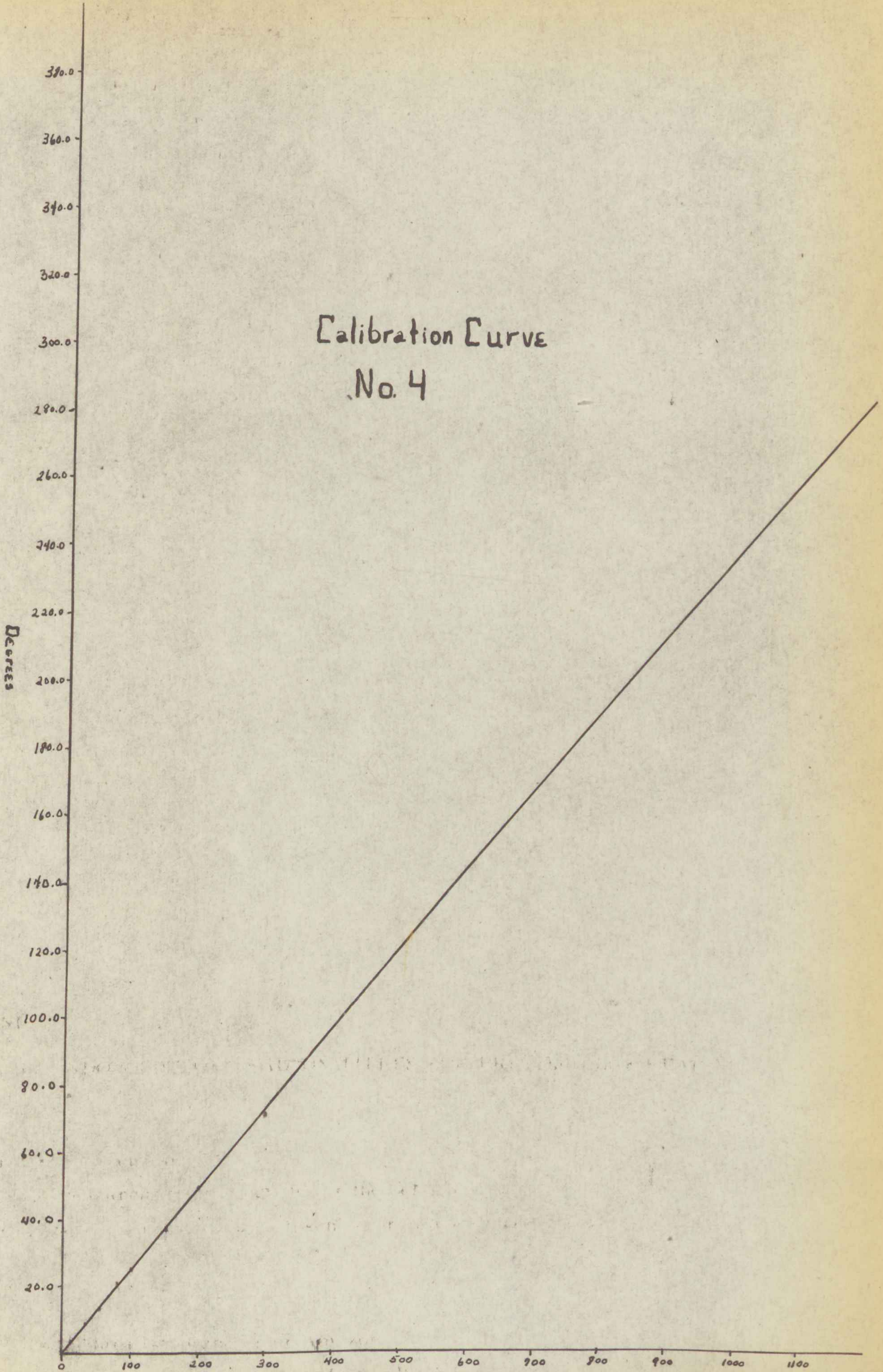

Calibration Curve
No. 1
Degrees
Milligrams
380.0
360.0
340.0
320.0
300.0
280.0
260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
0
100
200
300
400
500
600
700
800
900
1000
1100



Calibration Curve
No. 2



Calibration Curve
No. 3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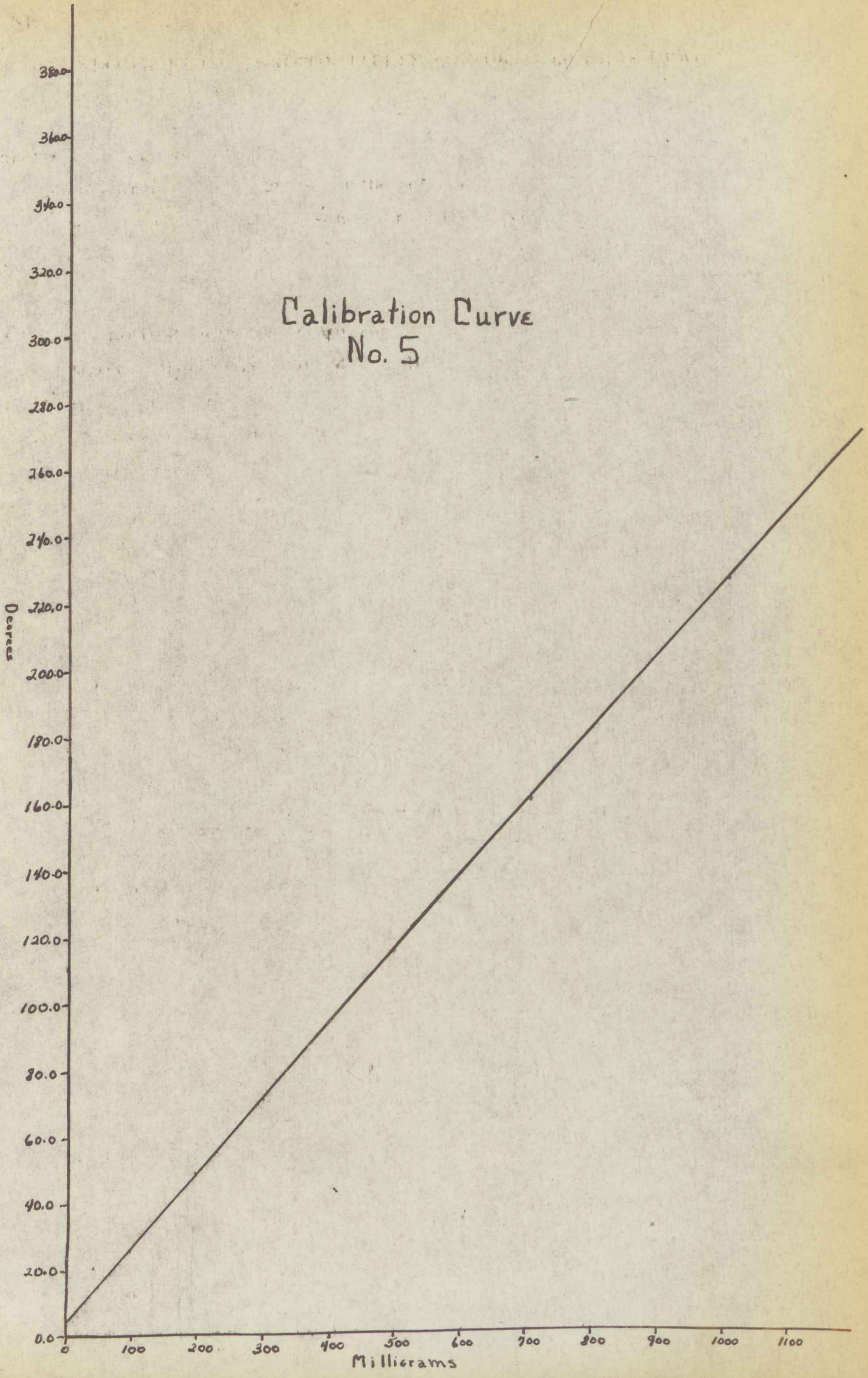
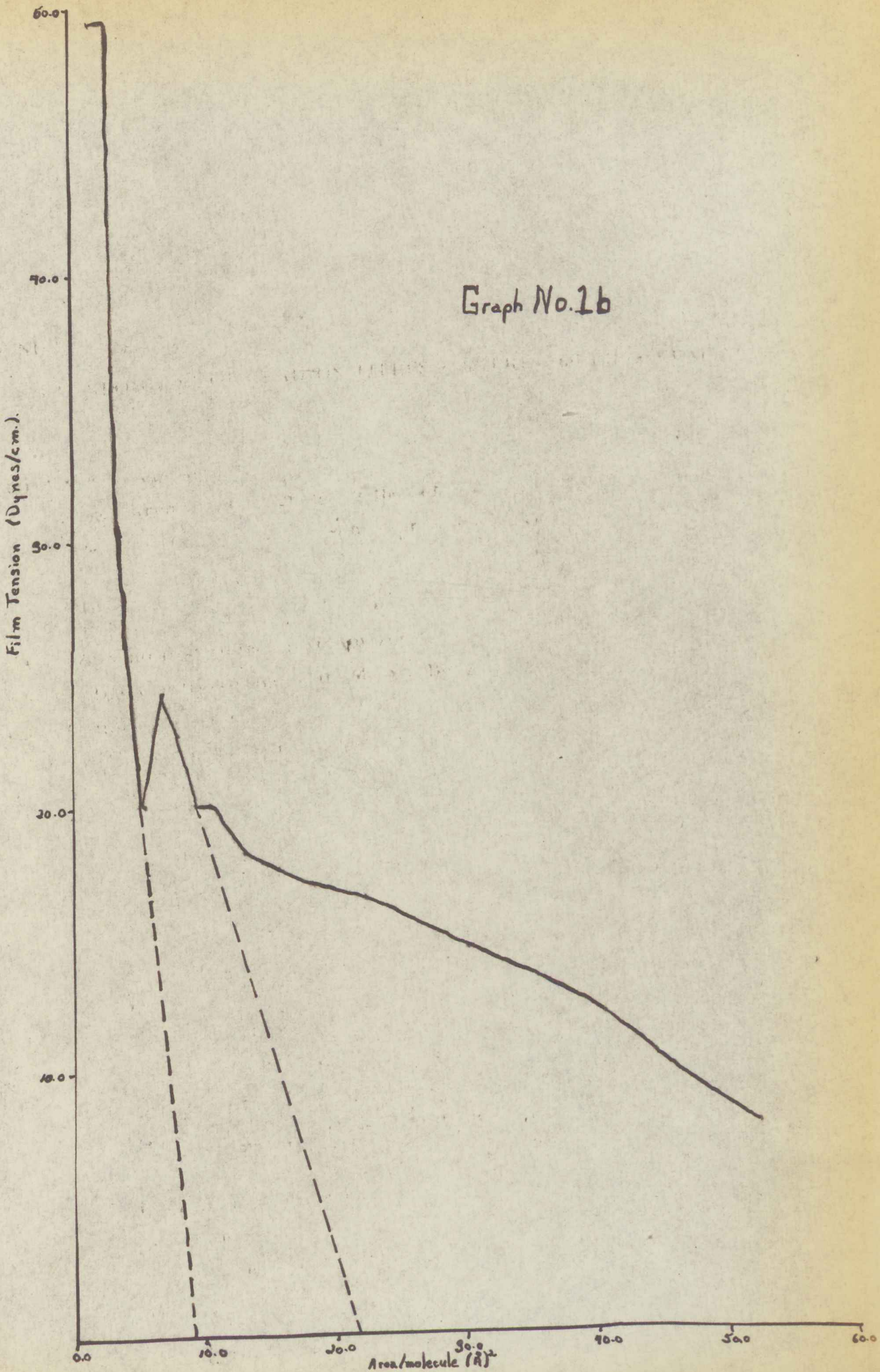
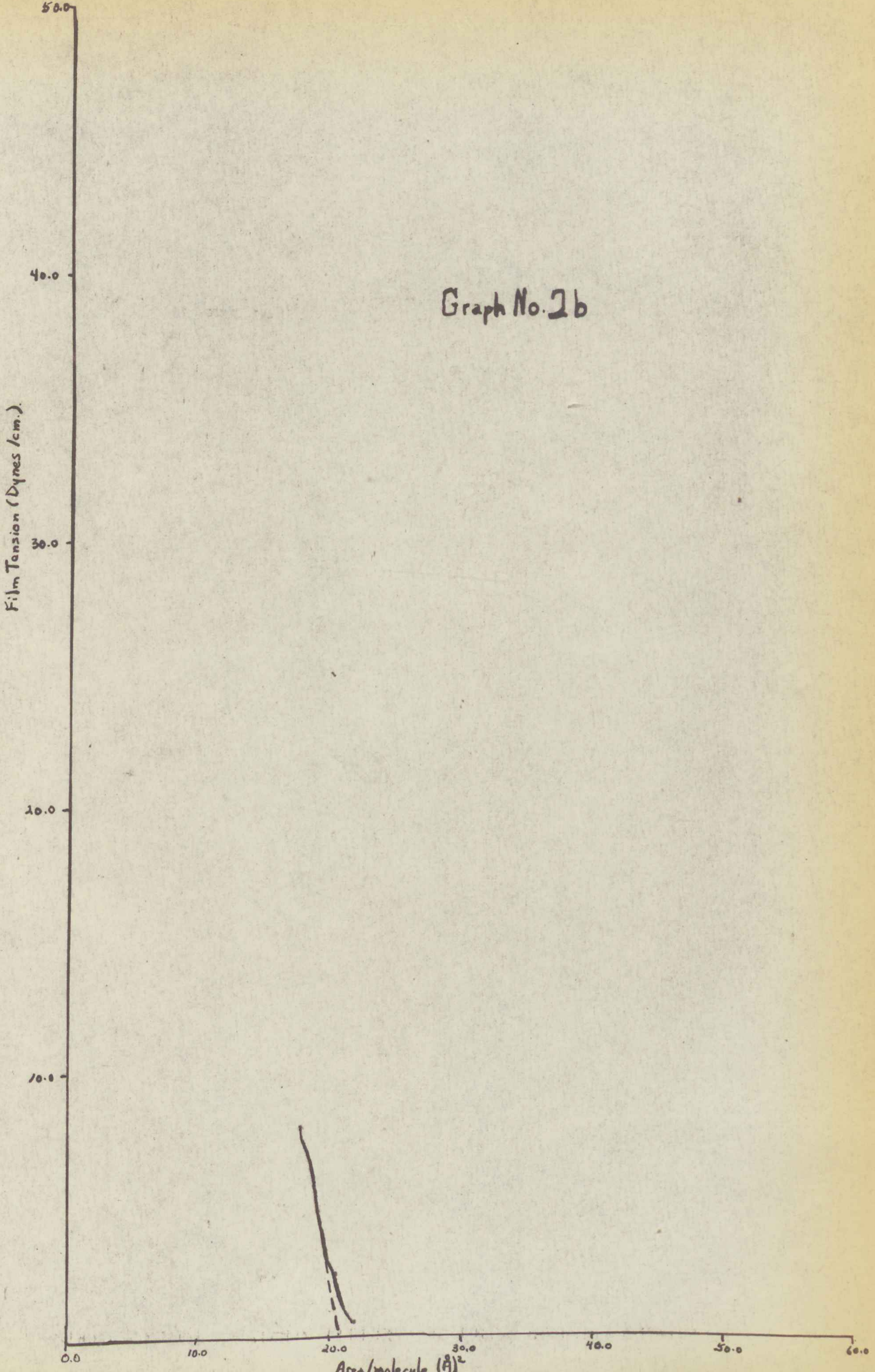
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
Degrees
0
100
200
300
400
500
600
700
800
900
1000
1100
Milligrams

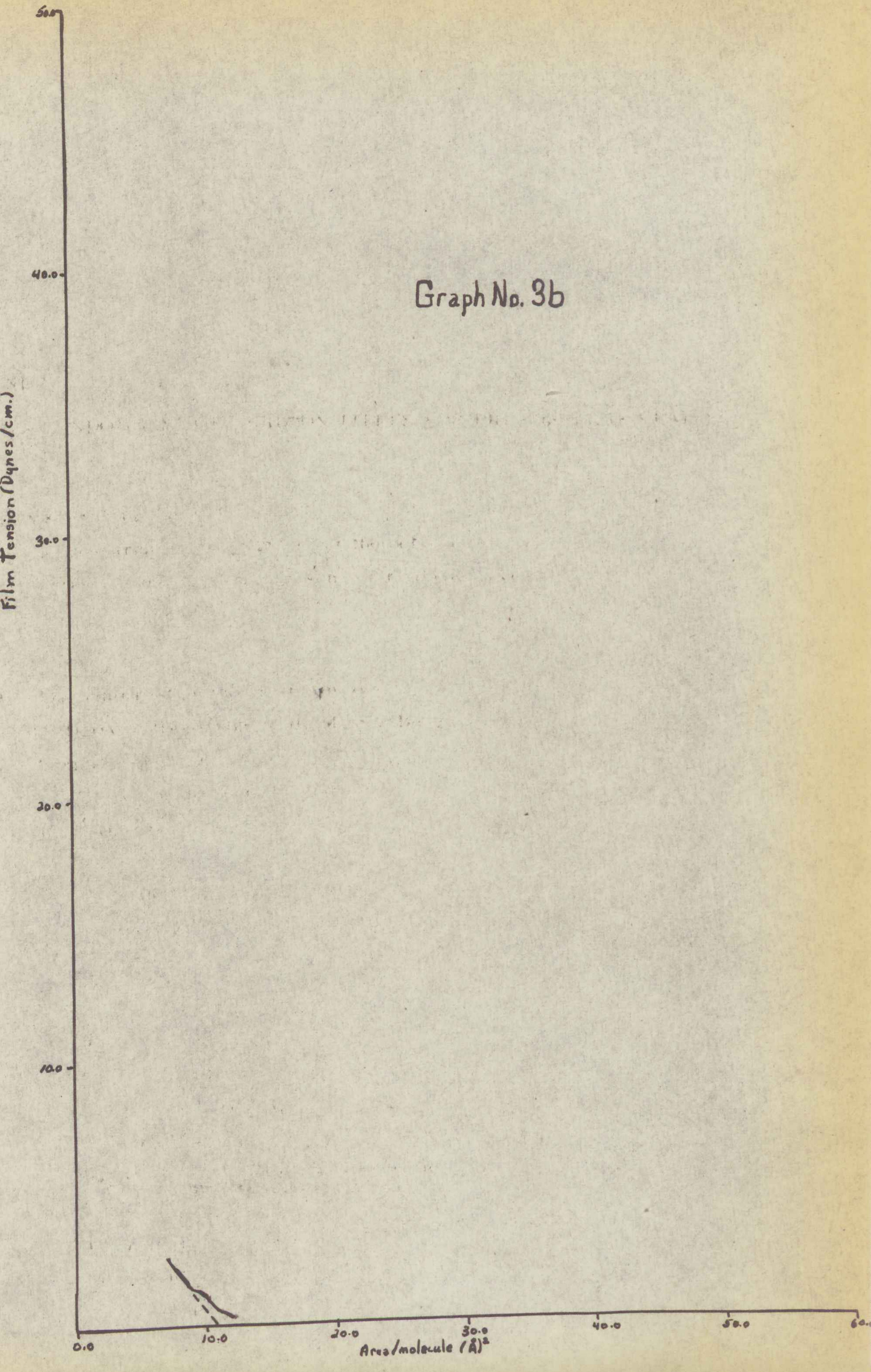


Calibration Curve
No. 5

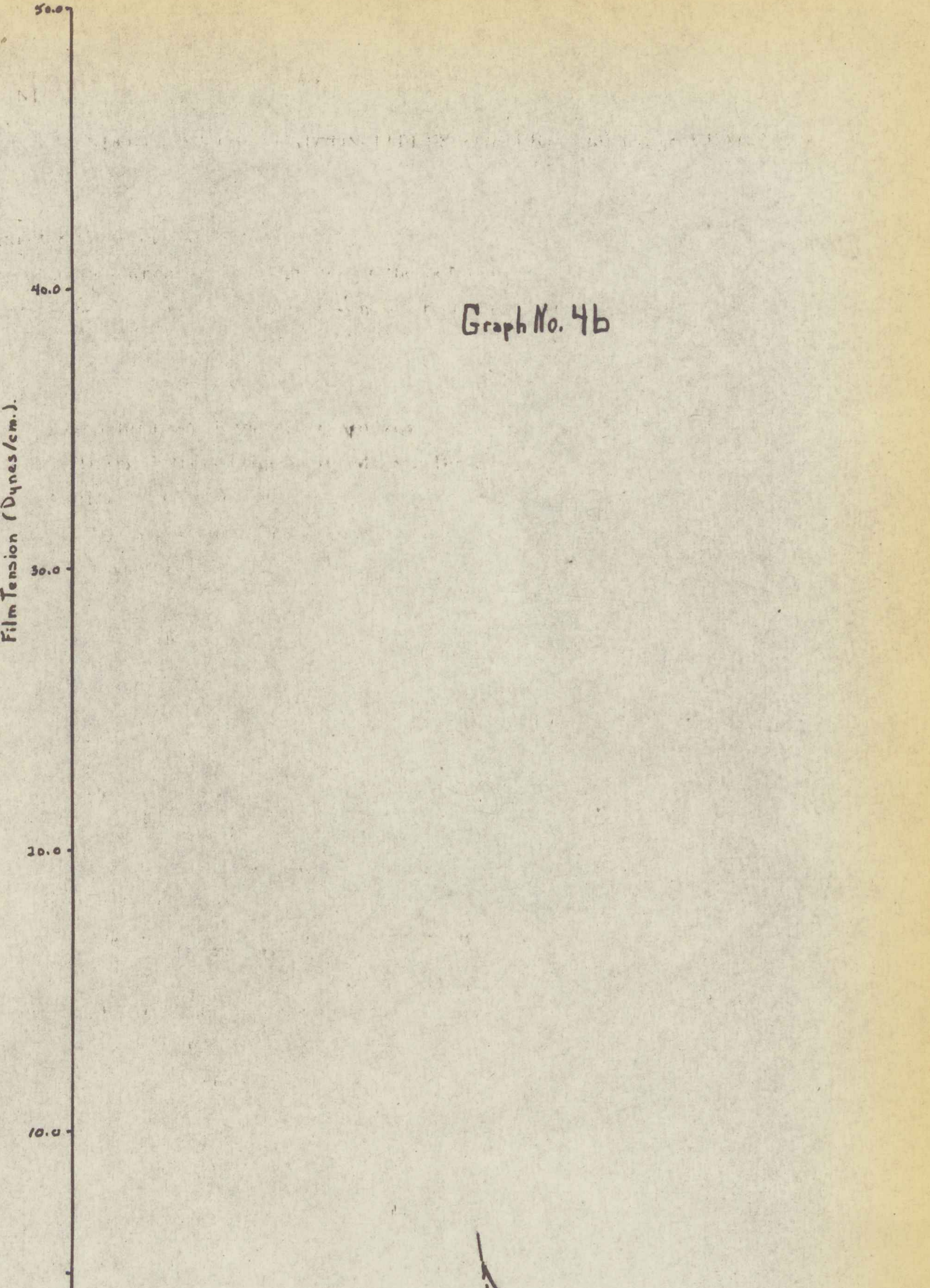

Graph No. 1b
Film Tension (Dynes/cm.)
50.0
40.0
30.0
20.0
10.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²



Graph No. 2b
50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes /cm.)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²


50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.)
0.0
10.0
20.0
30.0
40.0
50.0
60.
Area/molecule (Å)²

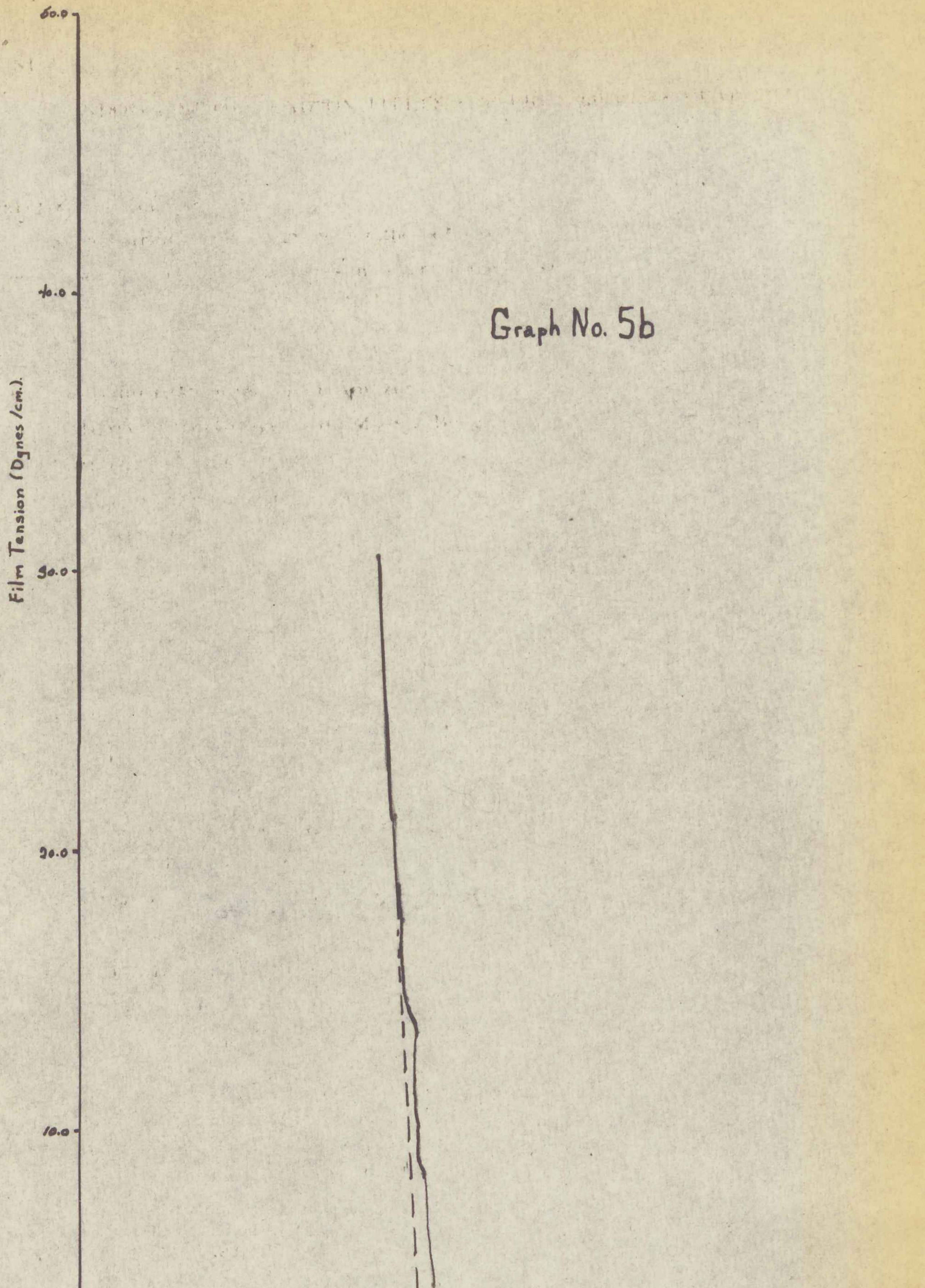
Graph No. 3b



Graph No. 4b

50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.).
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²

Graph No. 5b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40.0
30.0
20.0
10.0
Film Tension (Dynes /cm.)
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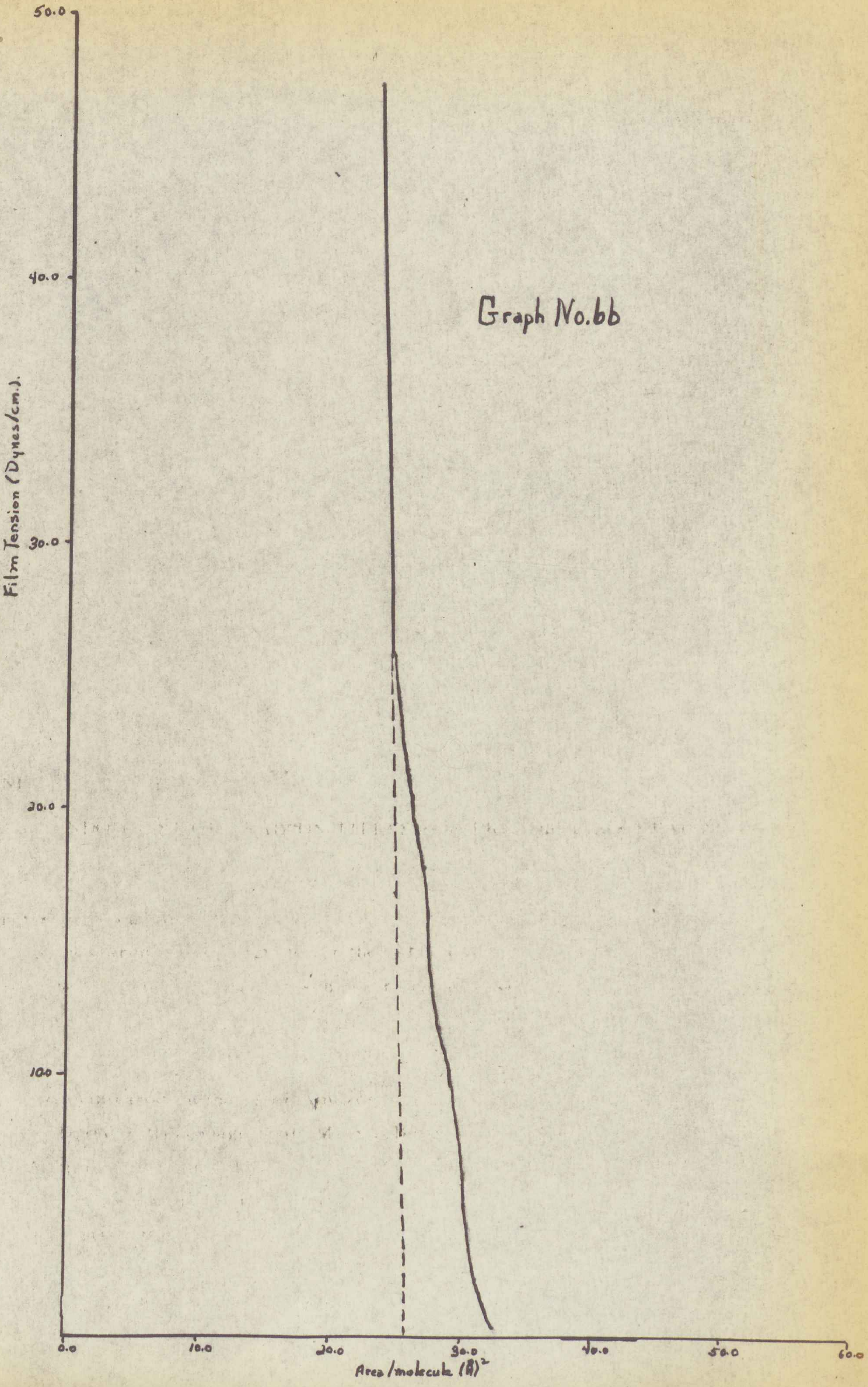
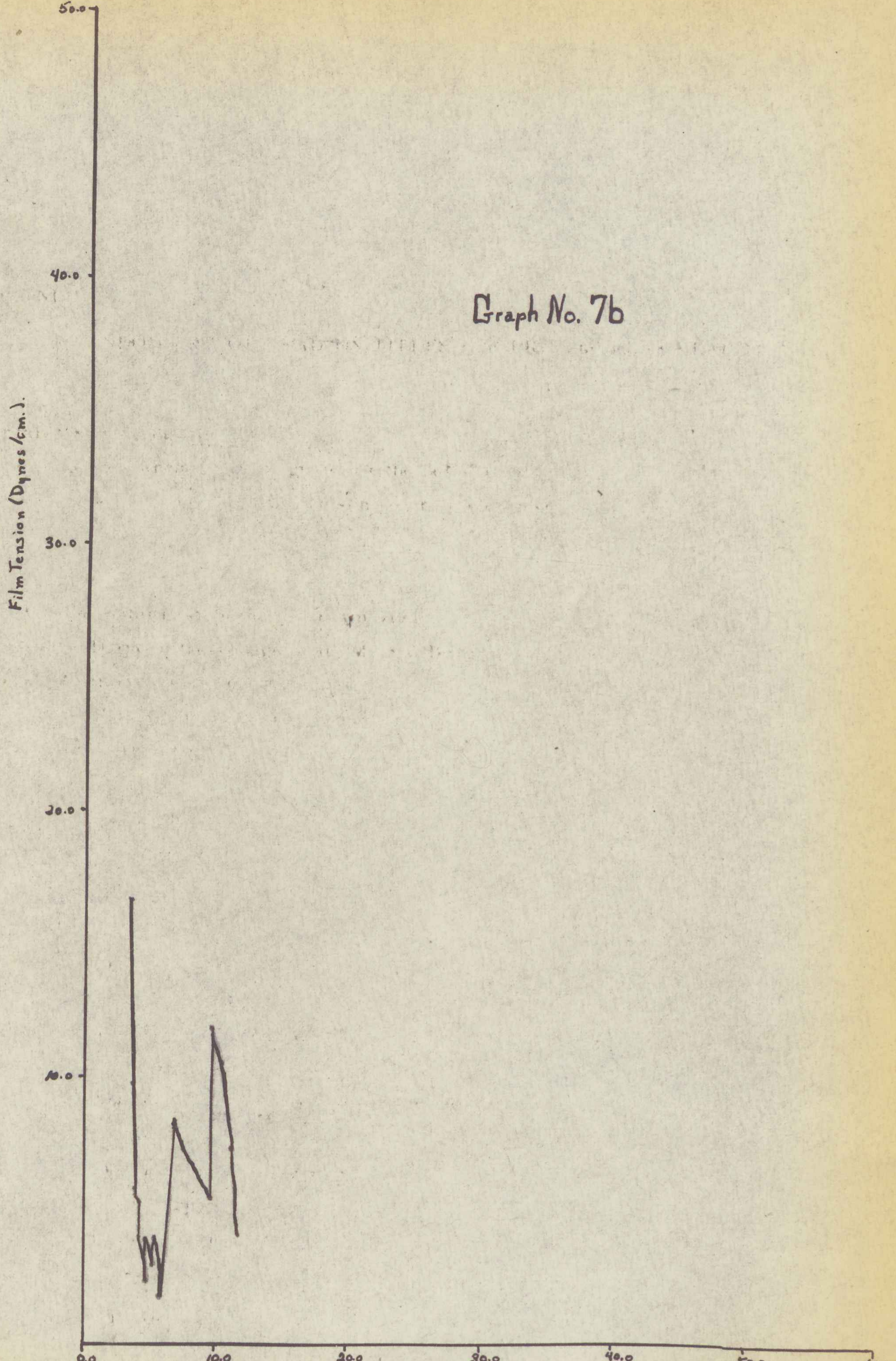
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)^2

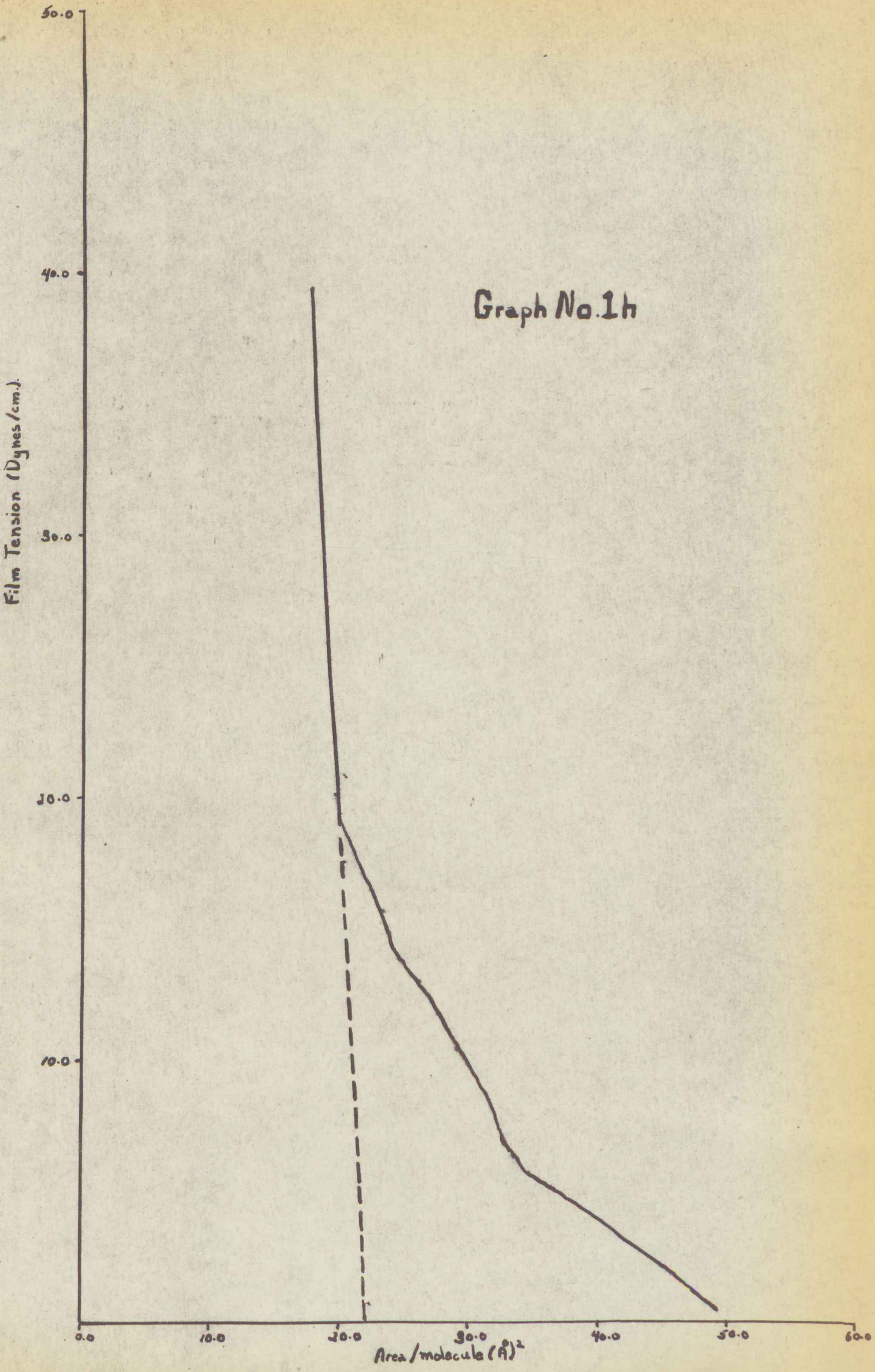


Graph No.66

50.0
40.0
30.0
20.0
100
Film Tension (Dynes/cm.)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²


50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.).
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²

Graph No. 7b


Graph No.1h

50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.)
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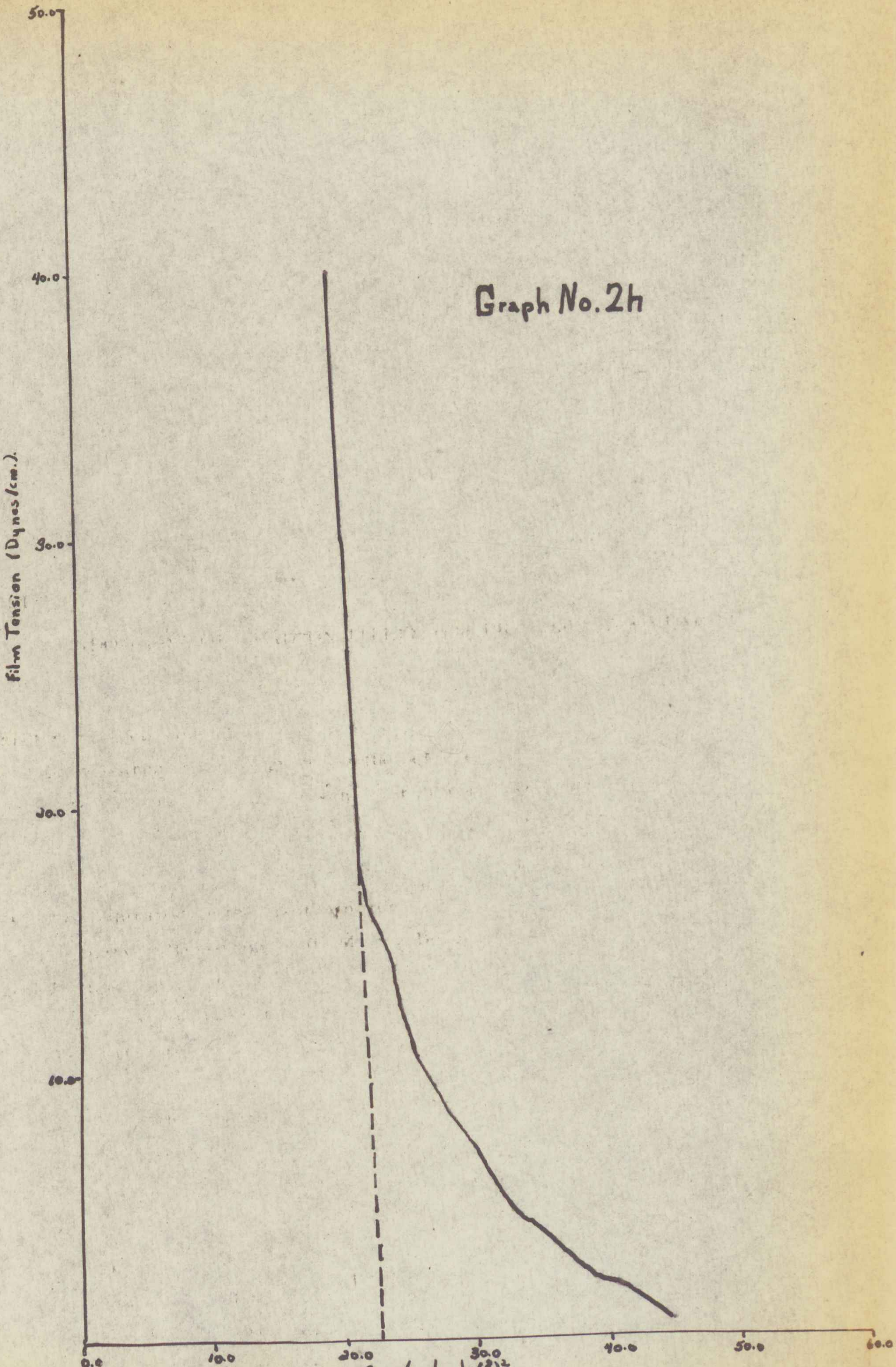
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²



Graph No. 2h

50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.)
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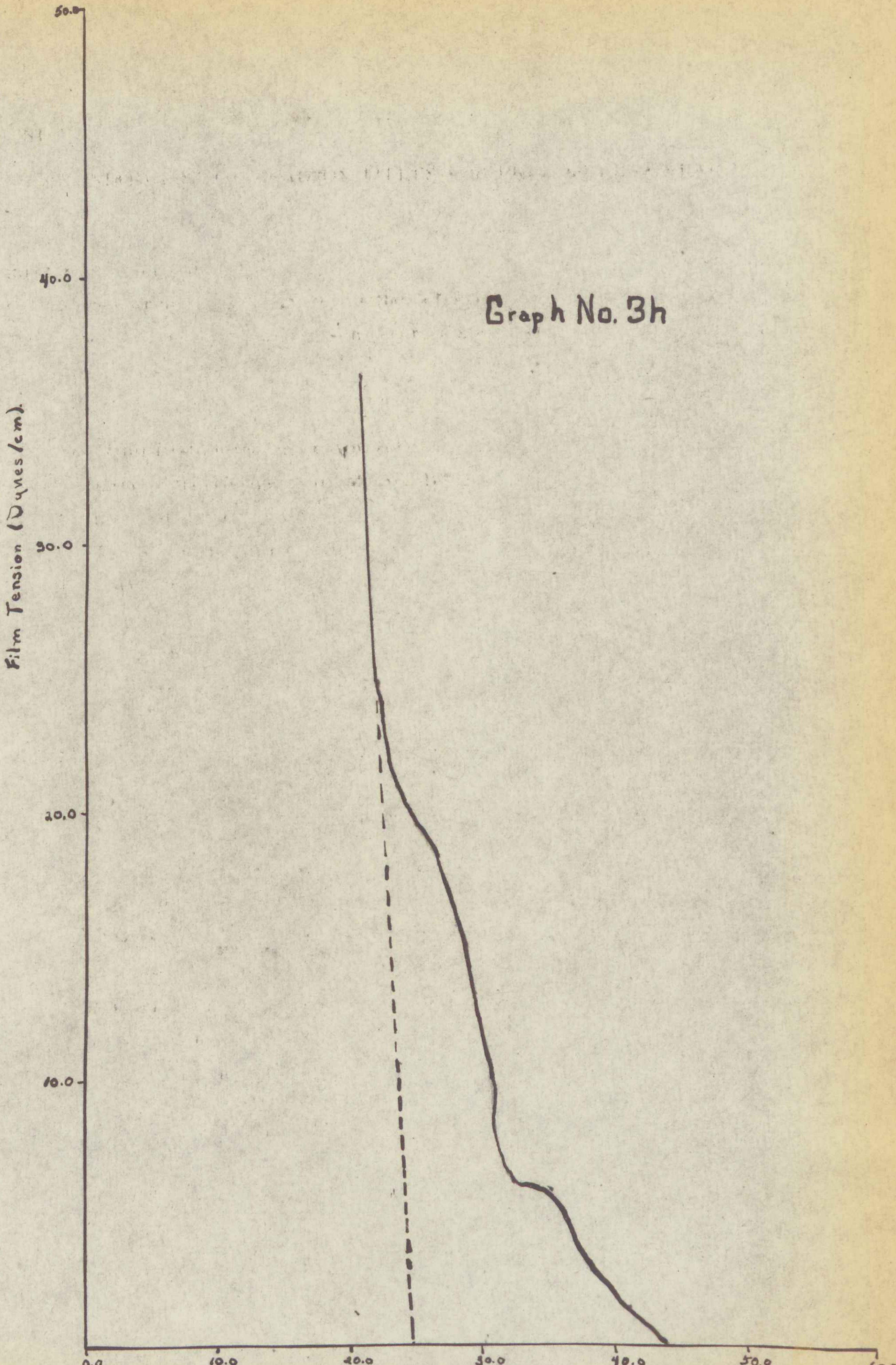
20.0
30.0
40.0
50.0
60.0
Area/molecule $(\text{Å})^2$

Graph No. 3h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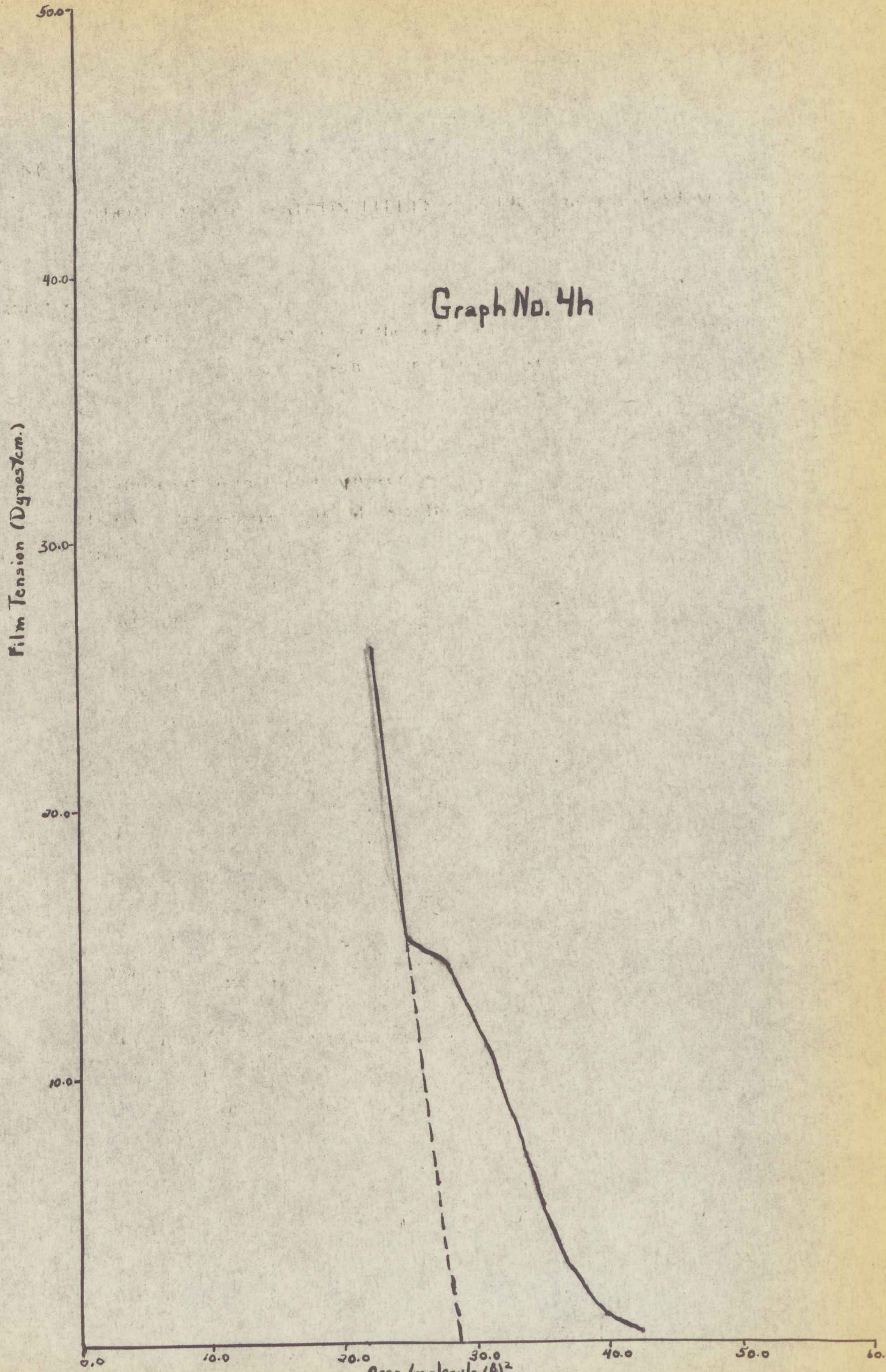
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²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30.0
20.0
10.0
Film Tension (Dynes/cm.)
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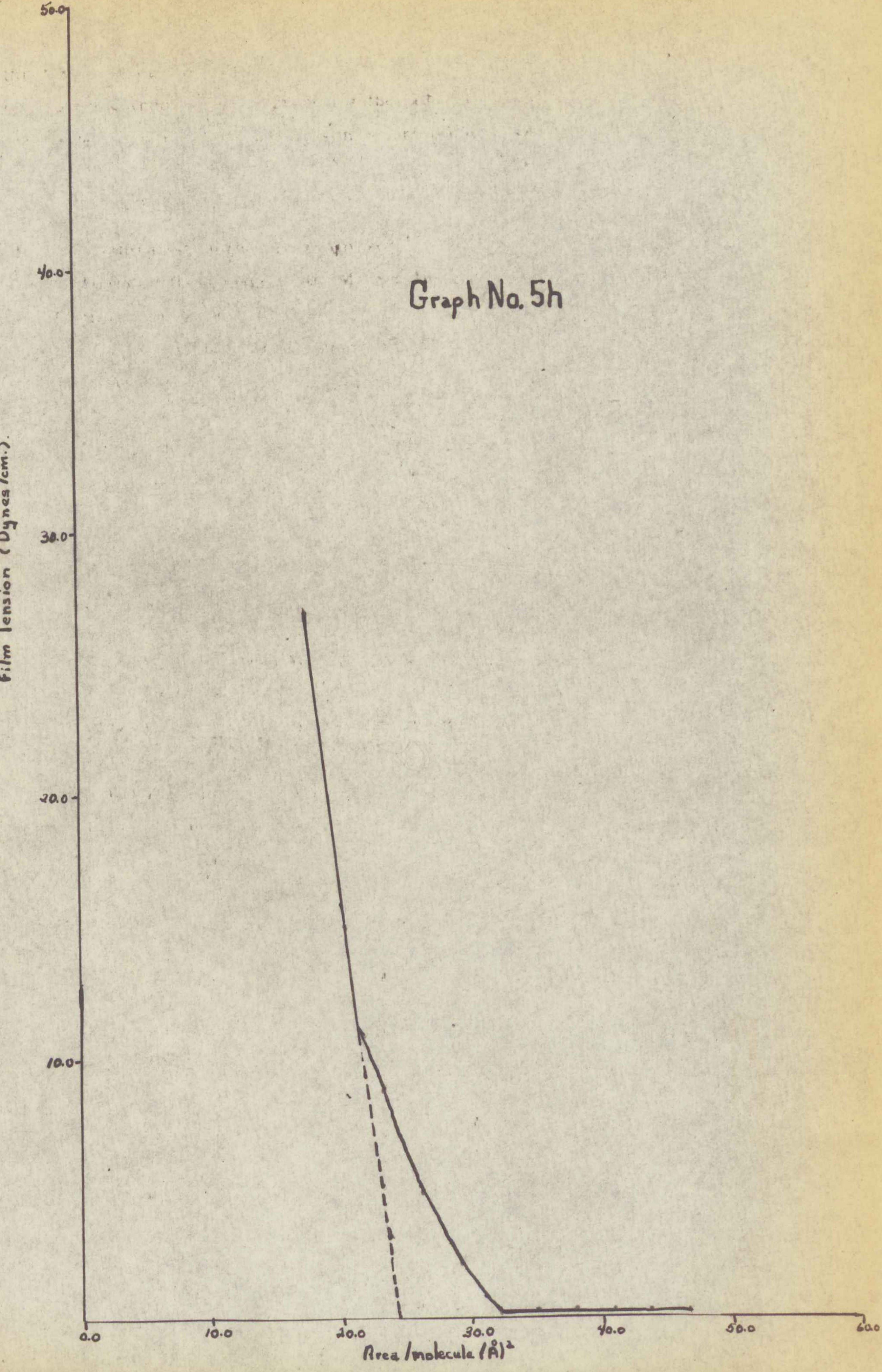
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)^2

Graph No. 4h


Graph No. 5h
Film Tension (Dynes/cm.)
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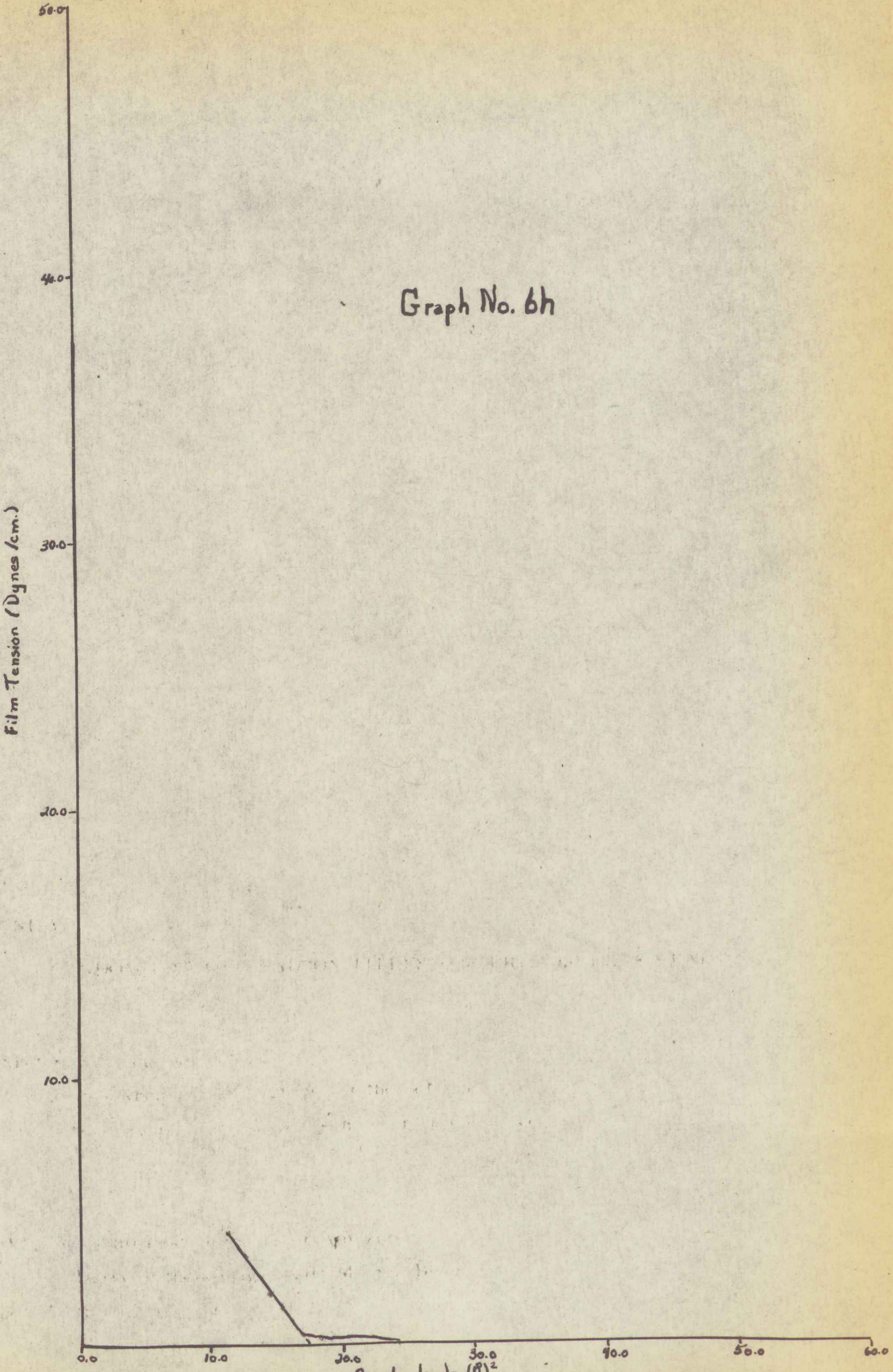
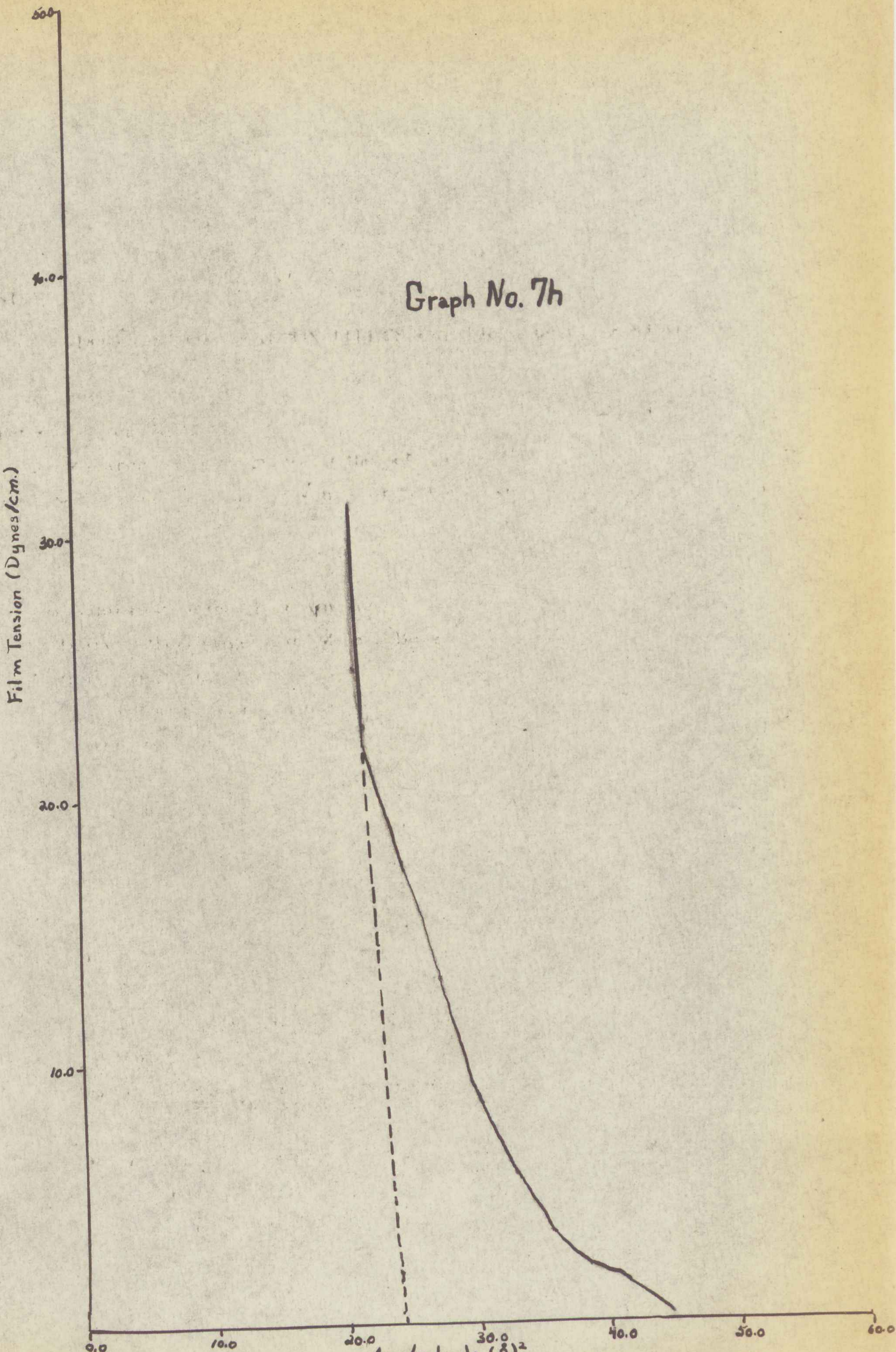
20.0
10.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²



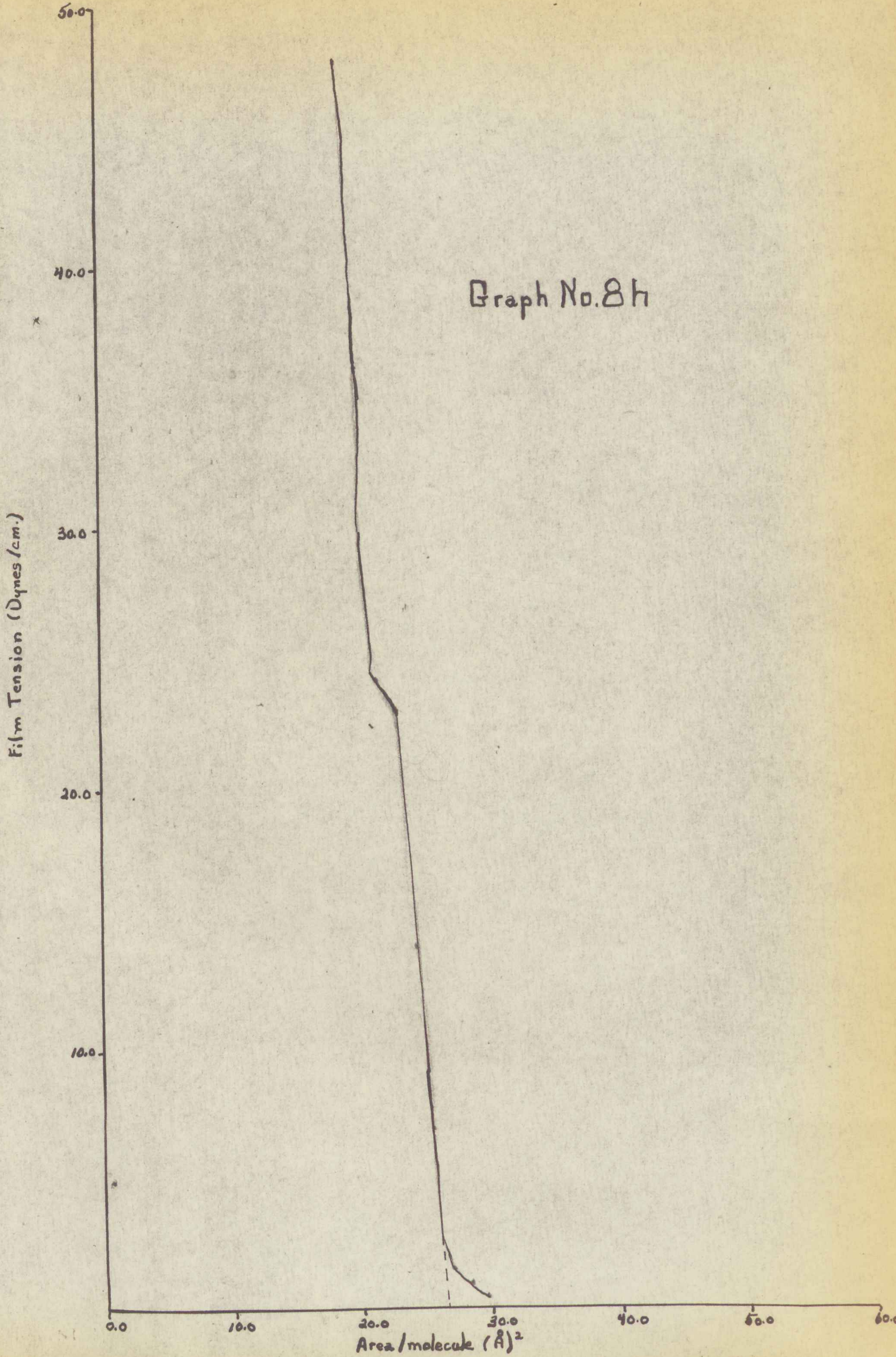
Graph No. 6h

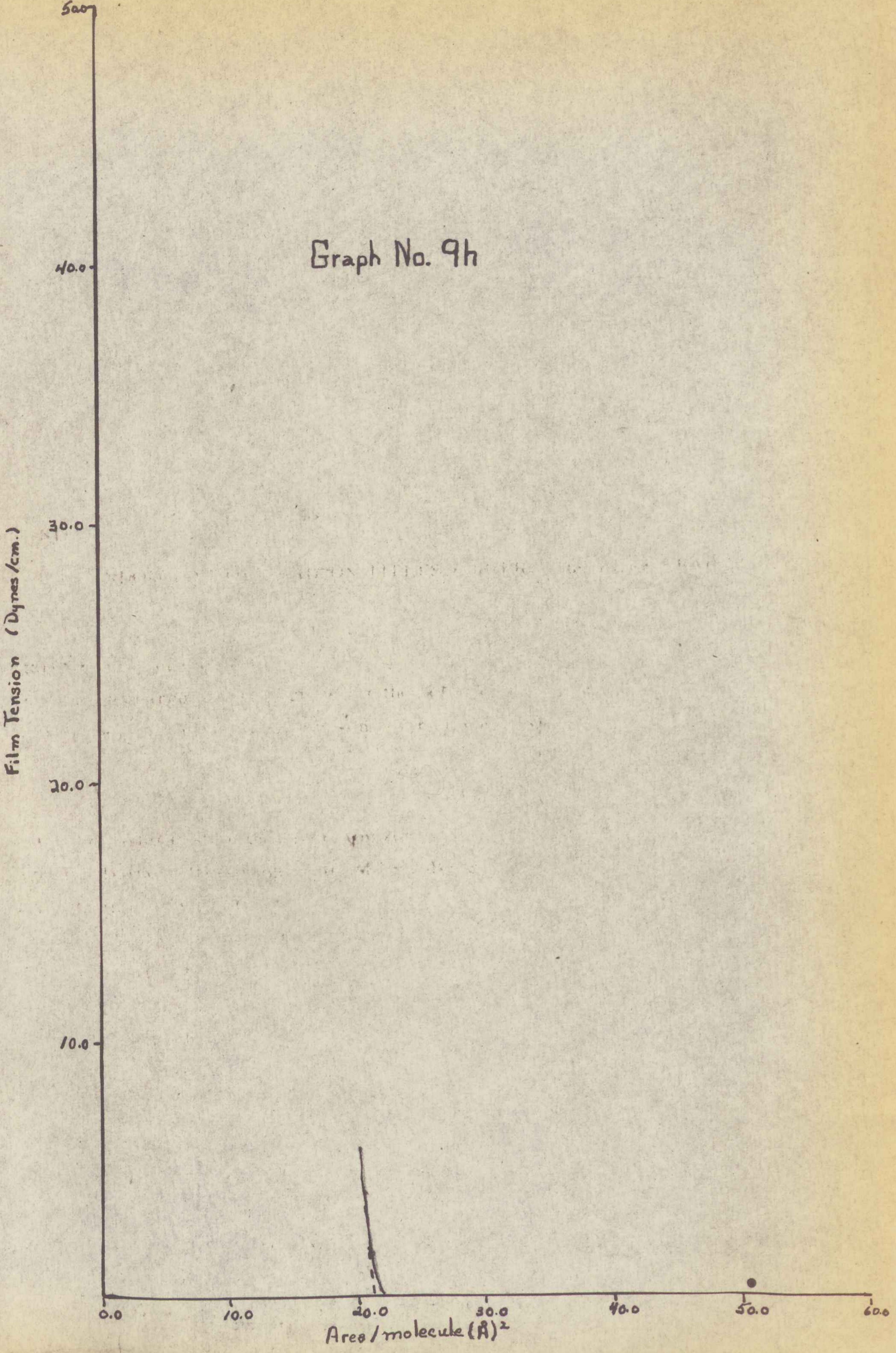
50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes /cm.)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²



Graph No. 7h

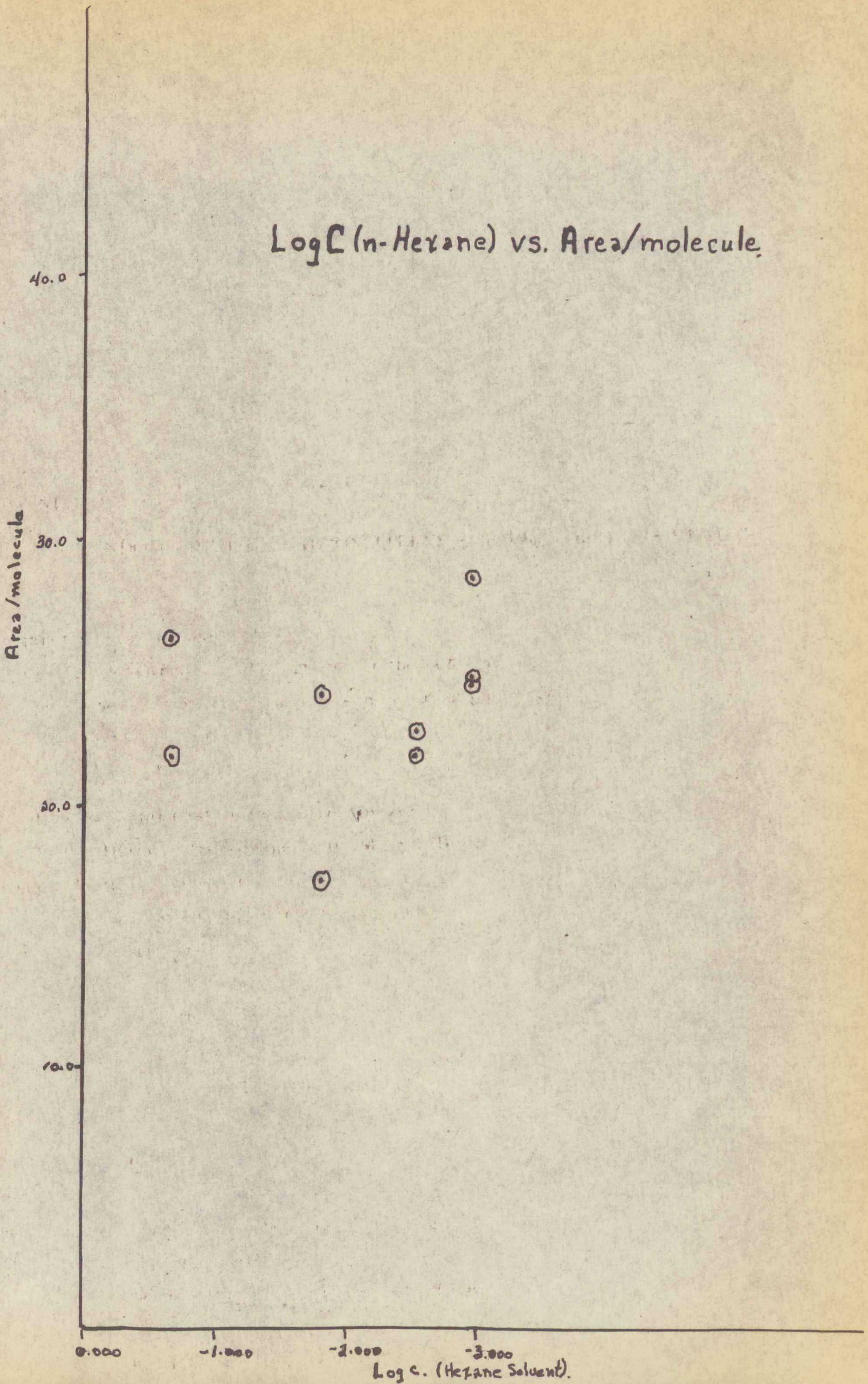
50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²


Graph No.8h
Film Tension (Dynes /cm.)
50.0
40.0
30.0
20.0
10.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area /molecule (Å)²



Graph No. 9h

50.0
40.0
30.0
20.0
10.0
Film Tension (Dynes/cm.)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Area/molecule (Å)²



LogC (n-Hexane) vs. Area/molecule