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SPECIAL REPORT

MOLECULAR WEIGHT DETERMINATIONS OF DIMETHYPOLY-SILOXANE POLYMERS

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ATOMIC ENERGY COMMISSION
UNITED STATES OF AMERICA

DEVELOPMENT DIVISION

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ABSTRACT

Using a Mechrolab Vapor Phase Osmometer and a Hallikainen Automatic Membrane Osmometer the number-average molecular weight of two samples of dimethylpolysiloxane - 2300 and 8000 cstk - as well as samples made by mixing the two previously mentioned materials were determined.

	Vapor Phase	Membrane
2300	~ 17,700	~21,500 ± 900
8000		~26,300 ± 300

The above values are in need of experimental verification in that they are the average values from the results of only four to six tests per sample. The experimental uncertainty accompanying these numbers (in this case the values are total range rather than standard deviation) indicates that the use of membrane osmometry to determine accurate number-average molecular weight for the dimethylpolysiloxane polymer is doubtful.

EXPLANATION OF NUMBER-AVERAGE

In the course of this investigation, it was noted that a cloud of ambiguity surrounds the terms number-average and molecular weights of polymers. Most polymers consist of a multitude of molecular species varying in size. To describe the polymer accurately, we must speak of a distribution of molecular size and weights. The broader the distribution, the greater the inhomogeneity of the particles. The diagram below represents a weight distribution of a typical polymer.[1]

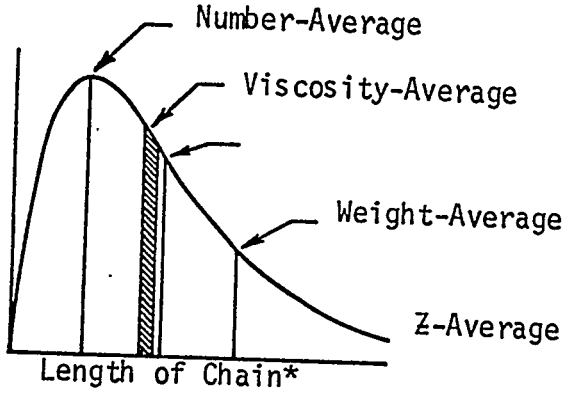


*Diagram from Billmeyer's Textbook of Polymer Science

To describe the distribution curve, we can refer to various experimentally accessible average molecular weights: number-average, weight-average, viscosity-average, Z-average, etc. Using a vapor phase or a membrane osmometer, a number-average is calculated, which is dependent only on the number of molecules, and not their size.

$$M_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

n_i = number of particles in i th interval

M_i = Molecular weight of the interval

[1] *Fred W. Billmeyer, Textbook of Polymer Science, New York: Interscience, 1965, P. 7.*

Vapor pressure lowering and osmotic pressure are colligative properties. Obviously the distribution is not unique to the value of M_n. Different samples of the same polymer with the same M_n may have different molecular weight distributions. Thus the number-average molecular weight for typical polymers at best indicates the position of the peak in the weight-distribution curve or the most provable molecular weight. To indicate the degree in inhomogeneity of the molecular weights (breadth of the curve, and thus determine whether the distribution has been shifted) the weighted average is needed. The weight-average molecular weight is dependent on the weight of the polymer in the molecular weight range and is defined as follows:

$$M_w = \frac{\Sigma\, w_i\, M_i}{\Sigma\, w_i}$$

w_i = weight of polymer

M_i = molecular weight of polymer

The breadth of the distribution is then roughly determined by the ratio of M_w/M_n and is only meaningful in a description of the breadth when the value is <4. A narrow distribution has a M_w/M_n close to 1, while a broad distribution is characterized by ratios greater than 2.

From examination of the formulae for M_n and M_w, it is obvious that they give emphasis to different portions of the distribution. Because the weight-average molecular weight is a weighted average, its value is more sensitive to the higher molecular weight species, and in general is always

greater than or equal to the unweighted average M_n. Any change in the distribution or amount of low molecular weight species will be noted readily in the calculation of M_n.

Earlier it was stated that the curve is not unique to a certain value of the M_n, and the same is true of M_w. However, while the distribution can be skewed, broadened or narrowed and still maintain the same number average molecular weight, the weight-average molecular weight will be different. The M_w acts as a cross check.

No one average molecular weight, whether it is the number average or the weight average, can fully characterize the distribution. Yet the two numbers together are invaluable in the description of the gross features of the molecular weight distribution curve.

PRINCIPLE OF MEASUREMENT IN VAPOR PHASE OSMOMETRY

The basis of the thermoelectric method is the principle of vapor pressure lowering. Any solution at a given temperature will have a vapor pressure lower than the pure solvent. Matched bead thermistors are used for detection, and on one is placed a solvent drop and on the other a drop of solution. The system is enclosed in an atmosphere of saturated vapor pressure isothermally maintained at T°K. Owing to different rates of solvent evaporation, solvent vapor will condense on the solution drop until the temperature is raised to some new T_1°K.

$$\ln \frac{P_1}{P} = \frac{-\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

The vapor pressure of the solution at T_1°K should now be equal to the vapor pressure of the solvent at T°K. The mathematical derivation of the formula used on the vapor phase calculations is given by S. Kume and H. Kobayashi[2].

In the solution the vapor pressure (correct for dilute solutions) or activity a_i of the solvent is lower than that of the pure solvent. The relationship between a_i and the resulting temperature difference $\Phi = (T_1 - T)$ is as follows:

$$(1) \quad \Phi = -\frac{RT^2}{H_0} \ln a_i \qquad \text{Clausius - Clapeyron}$$

R = gas constant

[2] *S. Kume and H. Kobayashi, Makromoleculare Chemie, 79, 1 (1964).*

H_0 = molar latent heat of vaporization at T°K

(2) $\ln a_i = - (M_1/M)\ c - (1/2 - X_1)\ (P_1/P_2)^2 c^2$ -----

M_1 and M are molecular weights of solvent and solute

P_1 and P_2 are the specific gravities of solvent and solute

X_1 = dimensionless constant

c = concentration (g/100 g of solvent)

To convert H to a resistance value ΔR

$\Delta R = q\ \Phi$

q = constant characteristic of the thermistor

(3) $\Delta R = Ac + g\ c^2$

$$\frac{\Delta R}{c} = A + gc$$

where $A = K/M$ $\quad K = \frac{qRT^2}{H_0}$ $\quad g = \frac{qRT^2}{H_0}\left(\frac{P_1}{P_2}\right)^2 (1/2 - X_1)$

H = latent heat of vaporation of solvent per 1 g at T°K

Therefore, in a plot of $\Delta R/c$ versus c, the intercept A equals K/M. By using a solute with a known molecular weight, K is calculated. Then the procedure is repeated with the unknown solute: with the new intercept and the value of K - the molecular weight is immediately determined M = K x A.

Thus, ideally the plot of $\Delta R/c$ versus c should be a straight line. Yet it is noted that the higher order terms in step 3 were dropped. In all but exceptional cases, this action is justified. Also observed values of ΔR vary with time. The drift is dependent on the solvent and the solute.

Mechrolab states that a 2 minute reading time for toluene is acceptable. However, for the higher molecular weight polymers, a ΔR versus Time curve should probably be plotted and extrapolated back to zero time.

DISCUSSION

Vapor Phase Osmometer: Procedure is in the Appendix.
The calibration constant was determined using solutions of anthracene in toluene at 37 °C (0.0058, 0.0088, 0.0196, and 0.0325 grams in five milliliters of toluene). These correspond approximately to the following molar solutions: 0.00652, 0.00987, 0.0220, 0.0365. The calculated value is K = 349.24, which was identical with the one determined earlier under Garland Barnes, former Pantex associate.

Using the K value based on the anthracene calibration, the molecular weights calculated for the polystyrene standard were from five to nine percent low. The equation used was $\Delta R/c$ vs c and no extrapolations to zero time were made. One must remember that the molecular weight of the standard is an average, and an insufficient number of tests were performed to determine whether the results would eventually cluster about 10,900. The prospects are doubtful because Mechrolab states that samples in the range of 10,000 to 20,000 have reported accuracies of five to eight percent.

Ideally once K is calculated for a given solvent and temperature, it should be the same for any solvent studied. However, for unexplainable reasons K often varies. Thus the author decided that the calibration should be performed with a polymer with a narrow molecular weight distribution - a silicone polymer being the most desirable. Since no silicone standards were available, Pressure Chemical Company's polystyrene standard (M_n = 10,900, M_w/M_n = 1.06) was substituted. The concentrations were expressed

in units of molality (grams of solute per 1000 grams of solvent) to avoid error in volume measurements. The K value finally used was an average of three results: K = 355.69 ohms - 1000 g solvent/mole. (The raw data and graphs are in the Appendix.)

Dilute solutions of the 2300 and 8000 samples of dimethylpolysiloxane were prepared and a summary of the tests are presented in Table I. The 8,000 sample never gave reproducible dekastat readings. Since the molecular weight of the 2,300 is greater than was expected (initially a value of 8,000 had been suggested), the calibration should be repeated with a standard closer to 20,000. However, Mechrolab and most experts do not recommend the vapor phase method for solutes with molecular weights greater than 18,000 to 20,000. The wide scattering of results may be due to the low concentrations used. All the dekastat readings were below 3 ohms. The reproducibility on repetitive readings is about 2-3% at readings less than 3 ohms (see Appendix). Sliemers of Battelle Laboratories advised in private talks, that for samples with molecular weights greater than 8,000, the extrapolation to zero time mentioned in the "Principle of Measurement" should be made. However, he was not too encouraging. So, since most sources discouraged further research, efforts to measure the number-average molecular weight were concentrated on the membrane osmometer.

Table I

Summary of Results - Vapor Phase Osmometry

I. Calibration Constant K = Molecular Weight of the Standard Times the Intercept $(\Delta R/c)_{C\to 0}$.

Standard	Run	$(\Delta R/c)_0$ ohms-1000g/g	K ohms-1000g/mole	Average K Value
Polystyrene	I	0.0331007	360.80	
Pressure Chem Co.	II	0.0325049	354.30	355.69
M_W = 10,900 ± 5%	III	0.0322903	351.96	

II. Number-Average Molecular Weight of Dimethylpolysiloxane (2300 cstk)

$M_n = K/(\Delta R/c)_{C\to 0}$ K = 355.69

Run	$(\Delta R/c)_{C\to 0}$	M_n	Average $\overline{M}_n$
I	0.021839	16,287	
II	0.020779	17,118	17,676
III	0.018127	19,622	

but $N_1 = 1-N_2$

so $\ln N_1 = \ln(1-N_2) = -N_2 + N_2^2/2 - N_2^3/3 + \text{-----}$

However, since N_2 is sufficiently small at high dilutions

$$-\ln N_1 = -\ln (1-N_2) = N_2$$

so $\pi V_1 = N_2 RT$

Furthermore $N_2 \simeq CV_1/M_n$

so as $c \to 0$

$$(\pi/c) = RT/M_n$$

$c \to 0$

c has units of g/100 ml of solvent.

R is the gas constant $848/\phi$, where ϕ is the density of the solvent at the manometer temperature.

$(\pi/c)_0$ designates the reduced osmotic pressure at infinite dilution.

π is in cm. of toluene[3].

Flory used statistical thermodynamics to derive the following relationship[4]:

$$\pi/c = RT/M_n + \Gamma_1 c + \Gamma_2 c^2 + \text{-----}$$

[3]*Paul J. Flory, Polymer Chemistry, Ithaca: Cornell University Press, 1953, P. 269 - 271.*

[4]*I bid., P. 512 - 513.*

$$\text{or} \qquad \pi/c = (\pi/c)_0 \left[1 + \Gamma_1^1 c + \Gamma_2^1 c^2 + \text{---}\right]$$

where Γ_1 & Γ_2 are constants

NOTE: The limiting case still holds $(\pi/c)_{c\to 0} = RT/M_n$

For most cases the higher order terms (> 1) can be neglected. Thus, a plot of π/c vs c is a straight line and extrapolation to infinite dilution ($c \to 0$) will give the intercept RT/M_n.

However, F. B. Rolfson & Hans Coll of Shell Development Company state that when using toluene better values are obtained if the quadratic term is not ignored. They assumed

$$\Gamma_2^1 = 0.25\Gamma_1^{1\,2}$$

thus enabling us to write

$$\pi/c = (\pi/c)_0 \left[1 + \Gamma_1^1 c + 0.25\Gamma_1^{1\,2} c^2\right]$$

$$\pi/c = (\pi/c)_0 \left[1 + \Gamma_1^1/2c\right]^2$$

If $(\pi/c)^{1/2}$ is plotted against c, again a straight line should be obtained which has a y-intercept equal to $(\pi/c)_0^{1/2} = (RT/M_n)^{1/2}$

DISCUSSION

Membrane Osmometer: Operating Temperature: 36.4°C, Solvent: Toluene

The procedure is in the Appendix.

For the polystyrene standard, the 2,300 and the 8,000 samples of dimethylpolysiloxane, both plots of (π/c) vs c and $(\pi/c)^{\frac{1}{2}}$ vs c are presented. In each case the extrapolation to zero concentration is performed. In Table II is a comparison of the values of M_n calculated from each intercept.

π/c vs c	$(\pi/c)^{\frac{1}{2}}$ vs c
$I = (\pi/c)_0 = (RT/M_n)$	$I = (\pi/c)_0^{\frac{1}{2}} = (RT/M_n)^{\frac{1}{2}}$

Even a cursory perusal of Table II and graphs (1-22) indicate that both plots give nearly the same molecular weight. However since the standard error of estimate in the y-co-ordinates is always at least a factor of ten less with the $(\pi/c)^{\frac{1}{2}}$ graphs than the (π/c) graph, the former is the better plot. The computer center has a least squares program for $(\pi/c)^{\frac{1}{2}}$ vs c.

Upon examining the graphs one notices that in some cases two values were reported - an extrapolated value based on an extrapolation back to time of closure of the sample outlet valve, and a value based on the average peak height within the first five minutes of the run. In general, extrapolation was applied only to the solutions of concentrations greater than 0.25 g/100 ml., since little solute permeation occurs with the low concentrations.

Examination of the charts of polystyrene indicate essentially no solute permeation (see Appendix). This was to be expected since the standard had a narrow distribution (Molecular Weight = 19,800, M_w/M_n = 1.06, and

Table II

COMPARISON OF PLOTS $(\pi/c)^{\frac{1}{2}}$ is c and (π/c) vs c

Sample	$(\pi/c)^{\frac{1}{2}}$ vs c		(π/c) vs c)	
	Sxy	M_n	Sxy	M_n
Polystyrene				
I	0.0054	18,621	0.0480	18,630
IV	0.0021	18,988	0.0221	18,994
V	0.0031	19,257	0.0250	19,272
Dimethylpoly-siloxane 2300				
I	0.0022	22,744	0.0160	22,755
II	0.00017	22,411	0.0015	22,414
III	0.0022	21,746	0.0160	21,751
IV	0.0070	21,726	0.0600	21,727
V	0.0180	24,444	0.1400	24,518
VI	0.0040	20,443	0.0370	20,446
VII	0.0020	20,697	0.0150	20,688
Dimethylpoly-siloxane 8000				
I	0.0053	26,298	0.0650	26,307
II	0.0084	26,481	0.0560	26,494
IV	0.0114	25,607	0.0520	25,635
V	0.0084	26,553	0.0570	26,561
VI	0.0084	26,342	0.0600	26,354

the 600 gel cellophane membrane is retentive to 7000). The values of M_n calculated appear to be low; however, more tests need to be run before it is evident what number they are clustering about.

The solute permeation in the 2300 and 8000 samples was significant and damaging only if the curve was allowed to run longer than seven minutes. The permeation was negligible at the low concentrations, which indicates that better results might be obtained if concentrations between 0.1 and 0.25 g per 100 ml. are used. For solutions above this range, if the test was run longer than 7 minutes, the solvent side of the cell became contaminated.

To verify the above statement, using the 8000 sample, the author preceded each concentration by a blank instead of another solution. Each time the osmotic pressure of the solution was higher than when it was run in the series (where the baseline is checked only before and after the series is run). The Shell Development Company, manufacturers of the Hallikainen Automatic Osmometer, states that if any solute permeation occurs, a blank should be run before each new polymer solution is introduced. However, the difficulty in reproducing a baseline makes this method too time consuming. So the author hoped by limiting the run time, the error would be alleviated. Consequently only the average values were used in the calculations of M_n.

In order to present the values with a reasonable uncertainty, the arithmetic mean of the results from the individual runs is reported, and then all the data points were plotted on a composite graph (Figures 7, 8, 14, 15, 26, 30, 34, & 38) and lines through the extreme high and low points

were drawn. The difference between the intercepts of these two lines was taken as the uncertainty range. The value of M_n finally quoted was the midpoint of this range ± one-half the interval. Table III consists of a summary of the number-average molecular weights for the 2300 and 8000 samples, as well as the mixtures. Using the average values of $\overline{M}_n$, attempts to determine the ratio of 2300 to 8000 in the mixtures proved meaningless.

Table III

NUMBER-AVERAGE MOLECULAR WEIGHTS - BASED UPON (π/c) vs c PLOTS

Sample	2300	8000	Mix #1	Mix #2	Mix #3	Mix #4
Average $\overline{M}_n$ of Test Results	21,631	26,270	22,275	23,211	21,772	21,797
Composite Plots Mol. Wt. Range	20,662-22,419	26,031-26,622	22,098-22,289	22,800-23,340	21,500-22,150	21,830-22,100
Mid Point of Range	21,540 ±880	26,316 ±285	22,193 ±100	23,070 ±270	21,825 ±325	21,965 ±135
Calculated Ratio 2300/8000	------	------	6.1	2	32.3	27.5

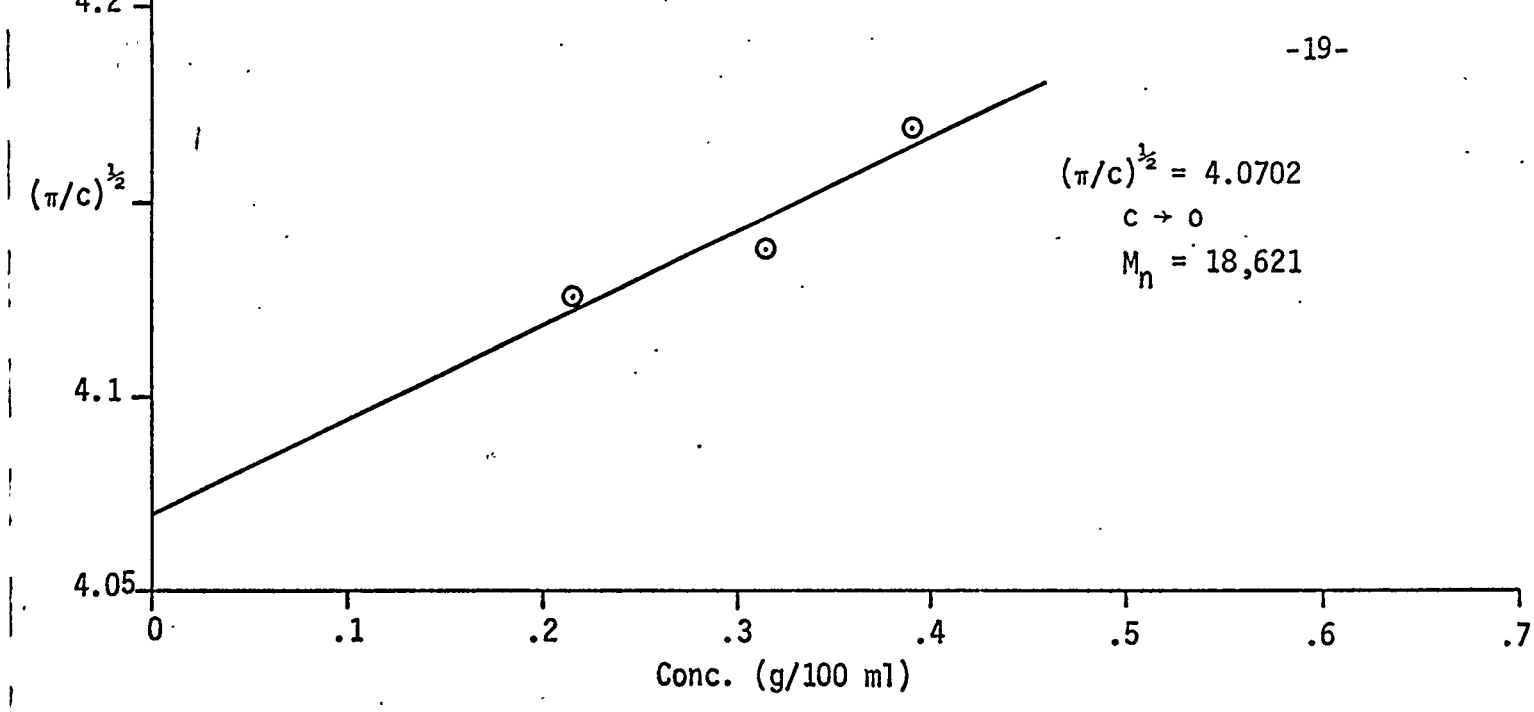


Fig. 1 Polystyrene Standard-RI

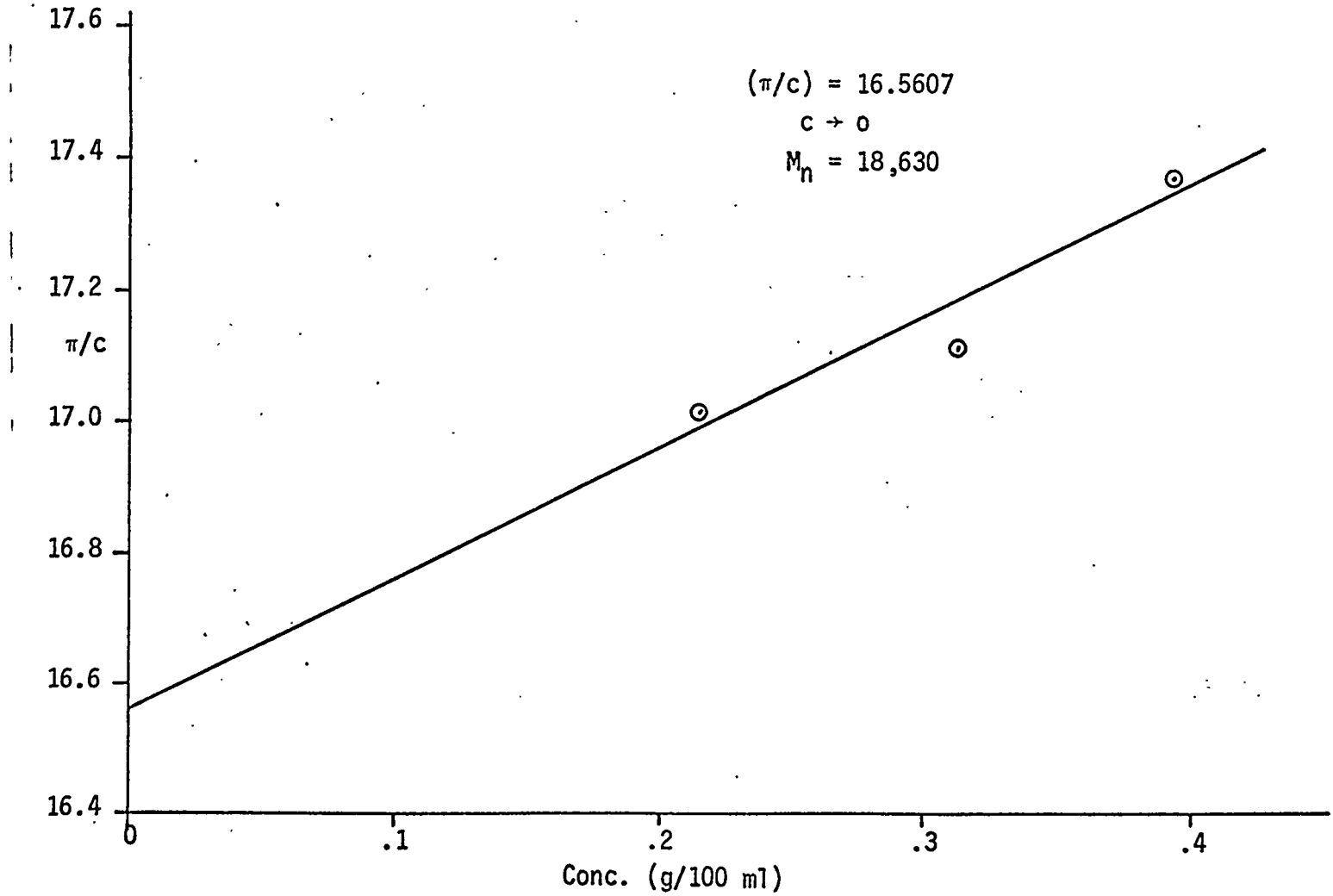


Fig. 2 Polystyrene Standard-RI

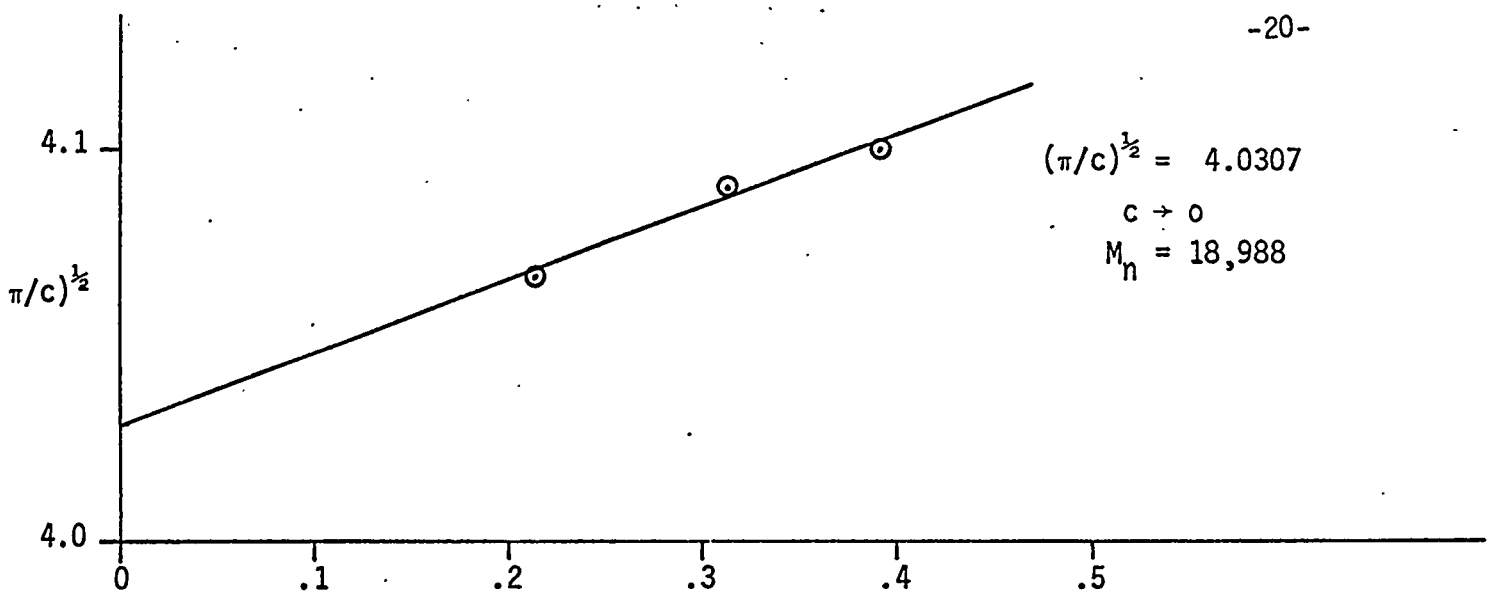


Fig. 3 Polystyrene Standard IV

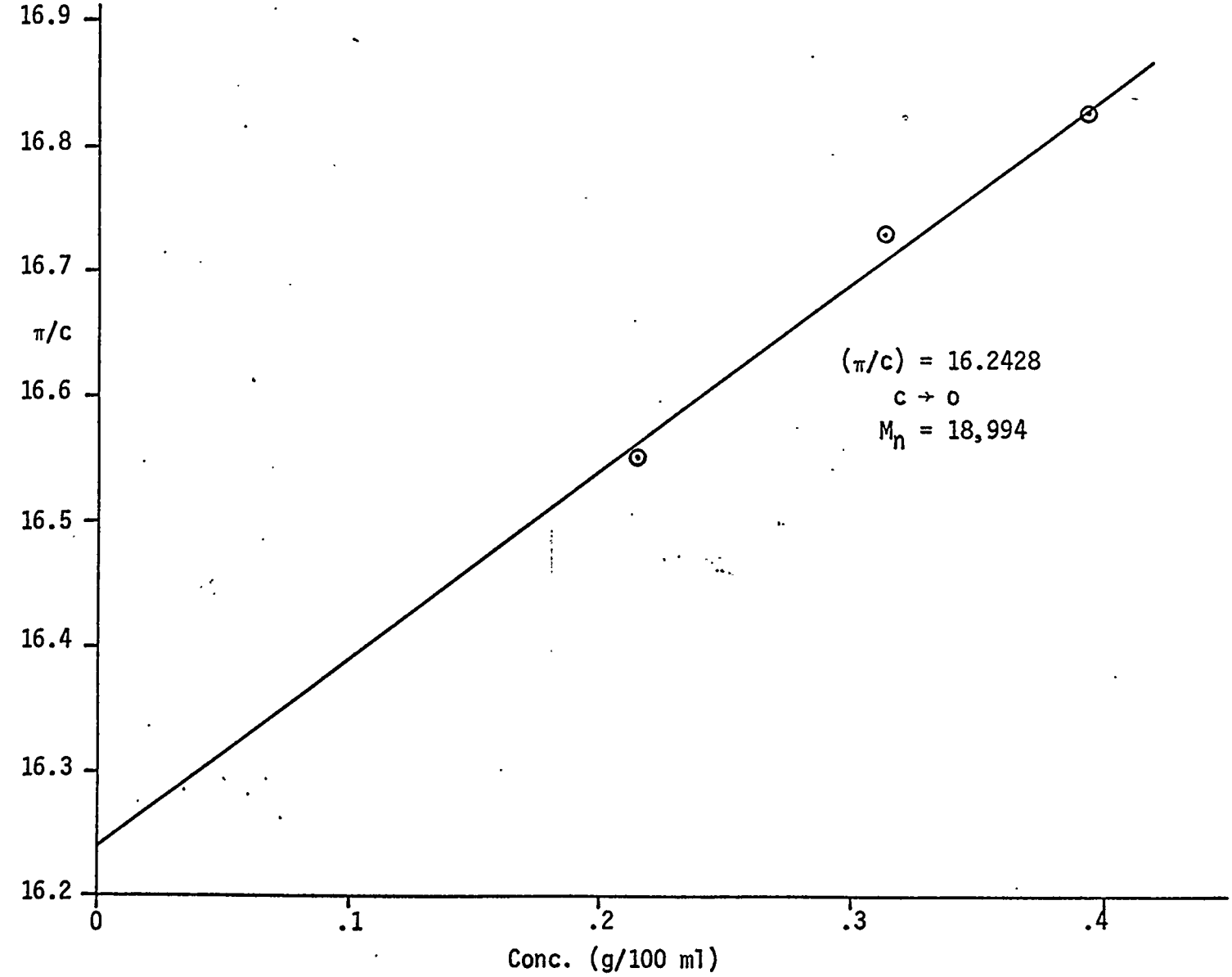


Fig. 4 Polystyrene Standard-RIV

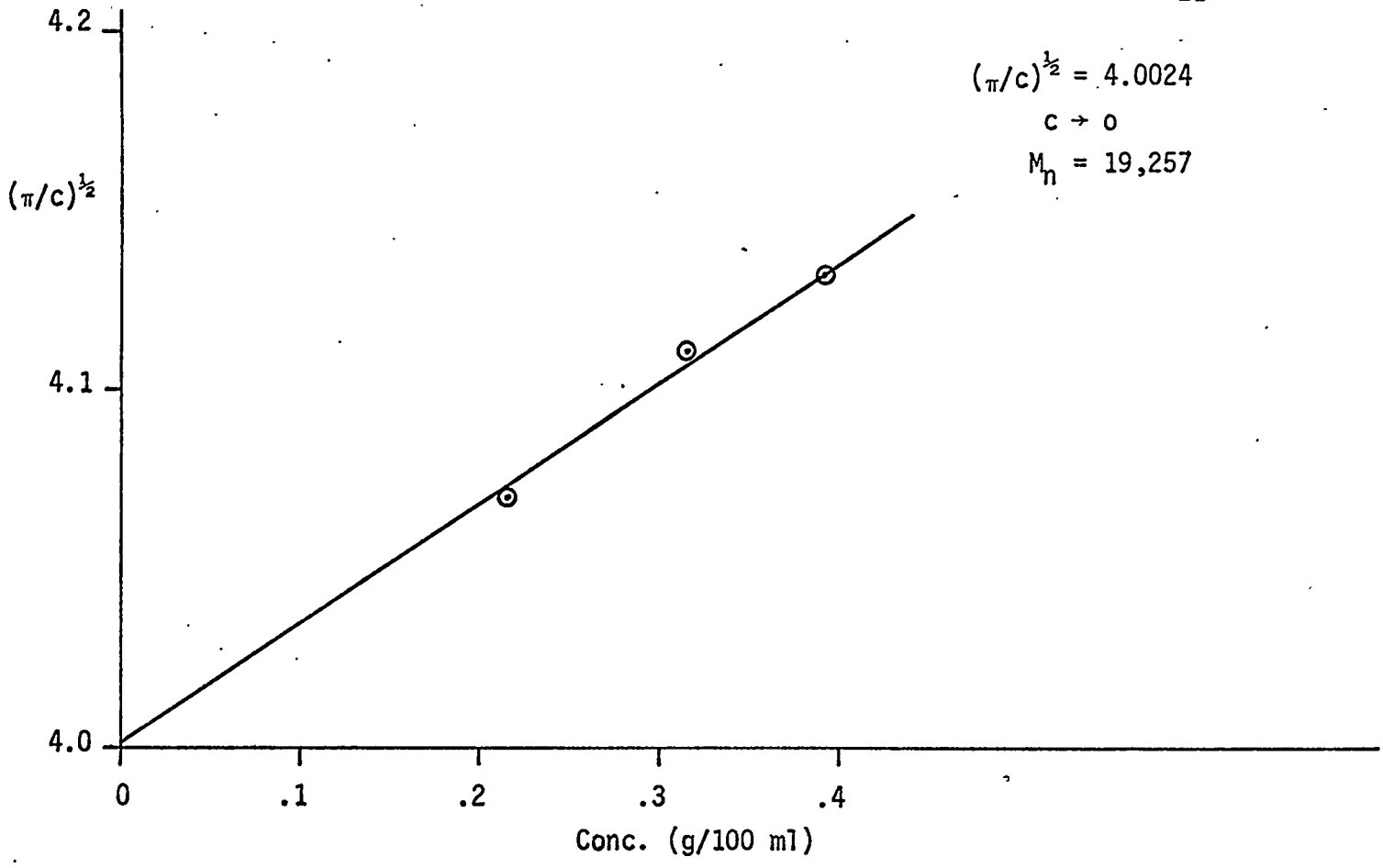


Fig. 5 Polystyrene Standard-RV

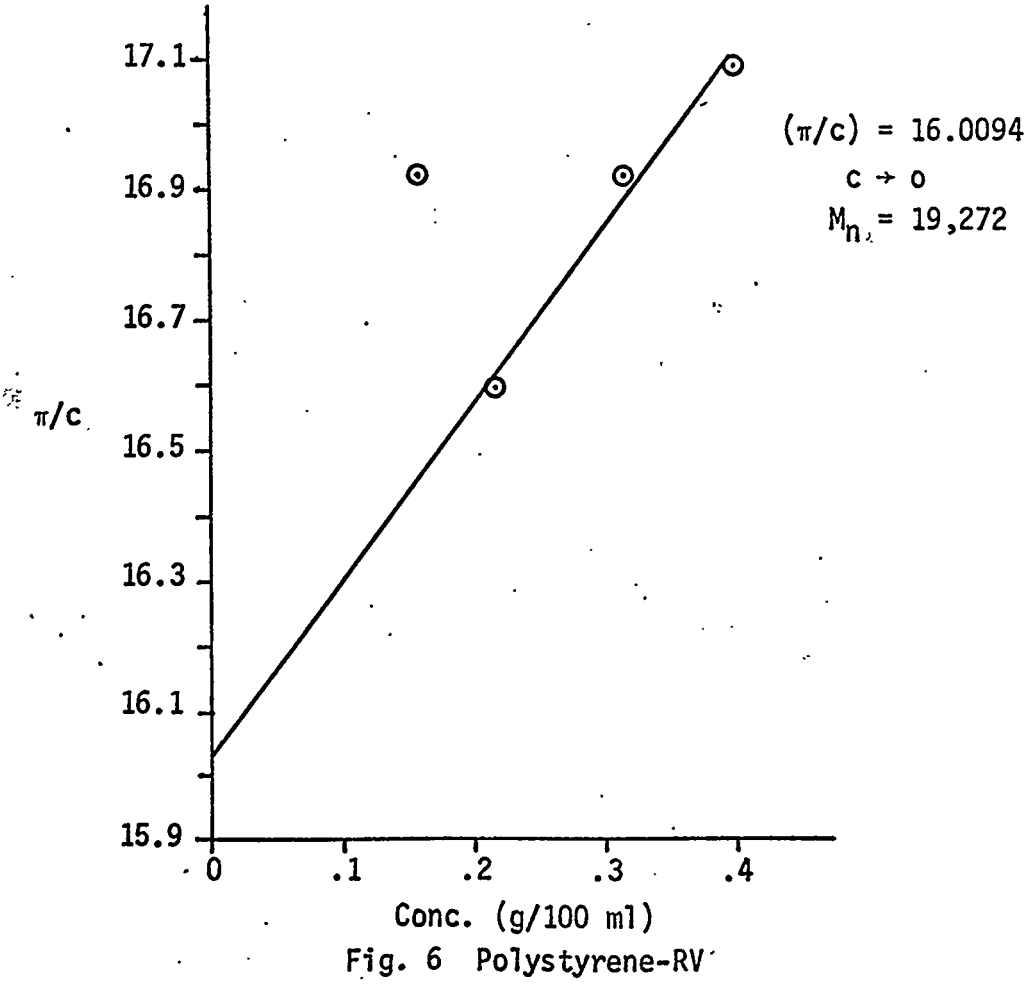


Fig. 6 Polystyrene-RV

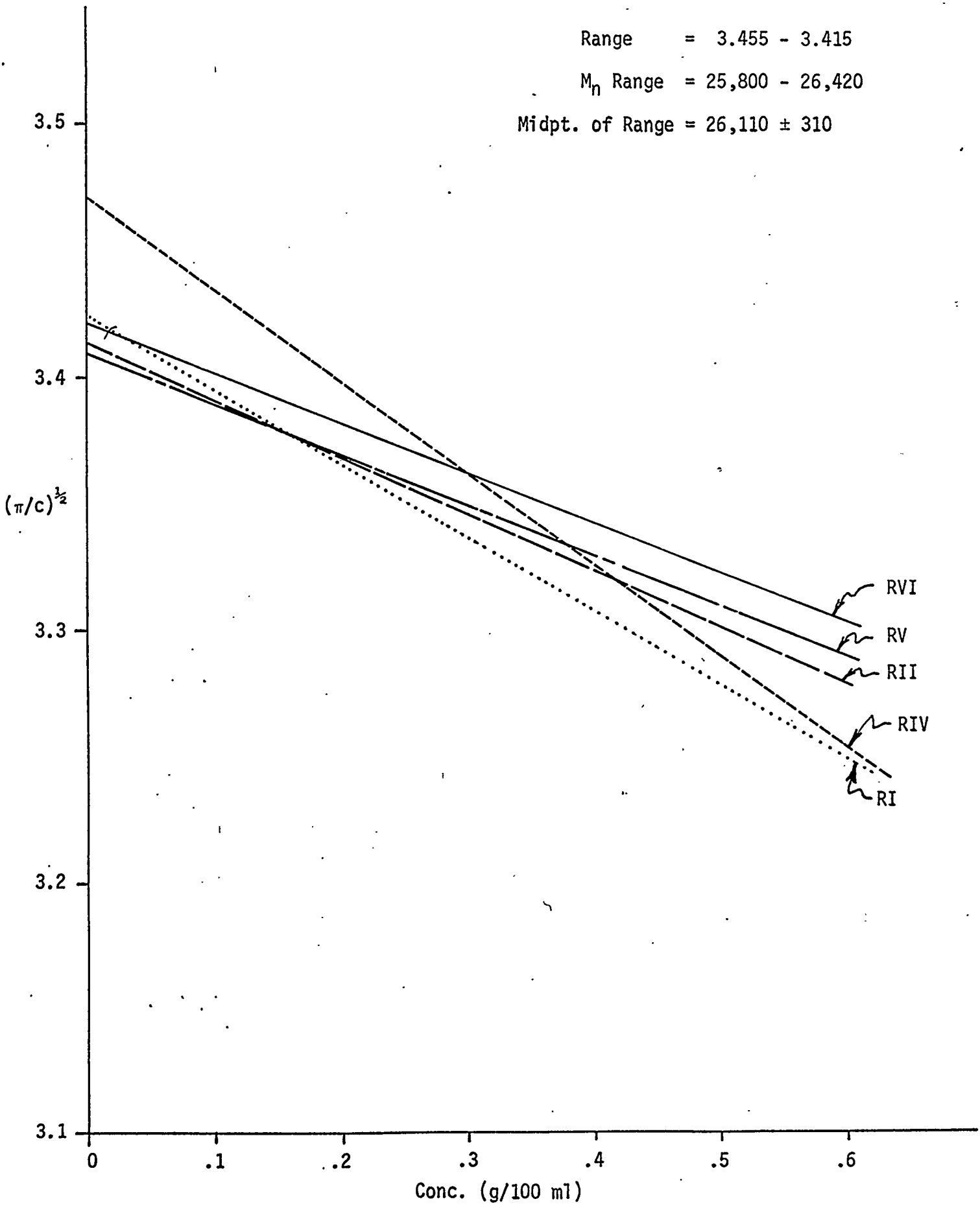
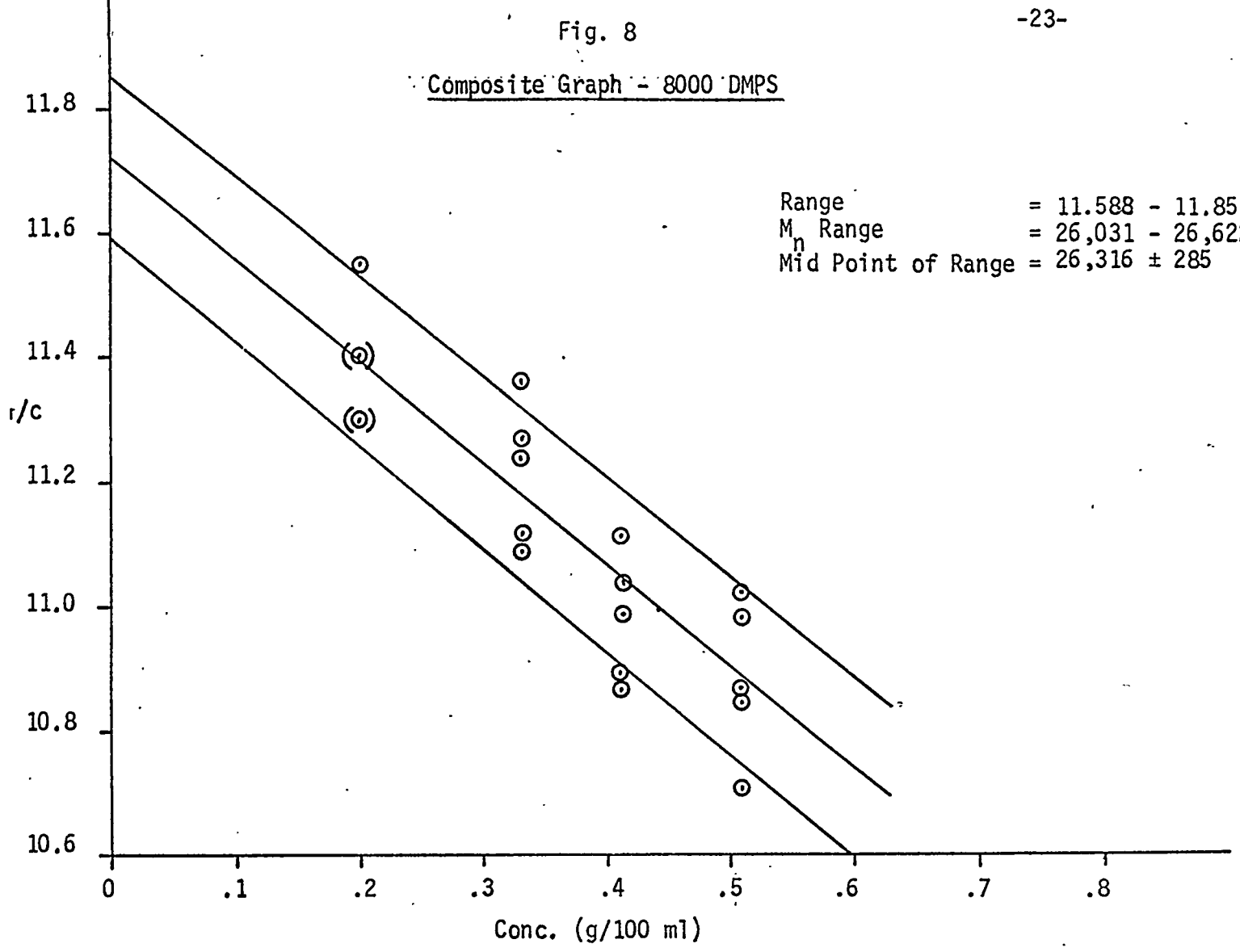


Fig. 7 Composite Graph for 8000 DMPS

Fig. 8

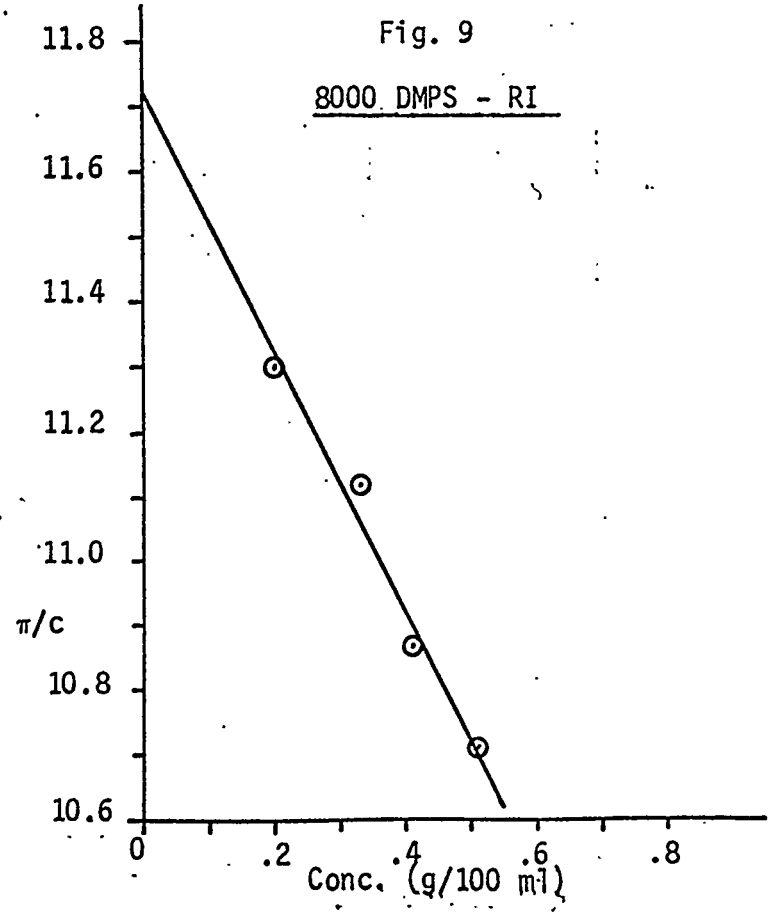
Composite Graph - 8000 DMPS



Range = 11.588 - 11.851
M_n Range = 26,031 - 26,622
Mid Point of Range = 26,316 ± 285

Fig. 9

8000 DMPS - RI

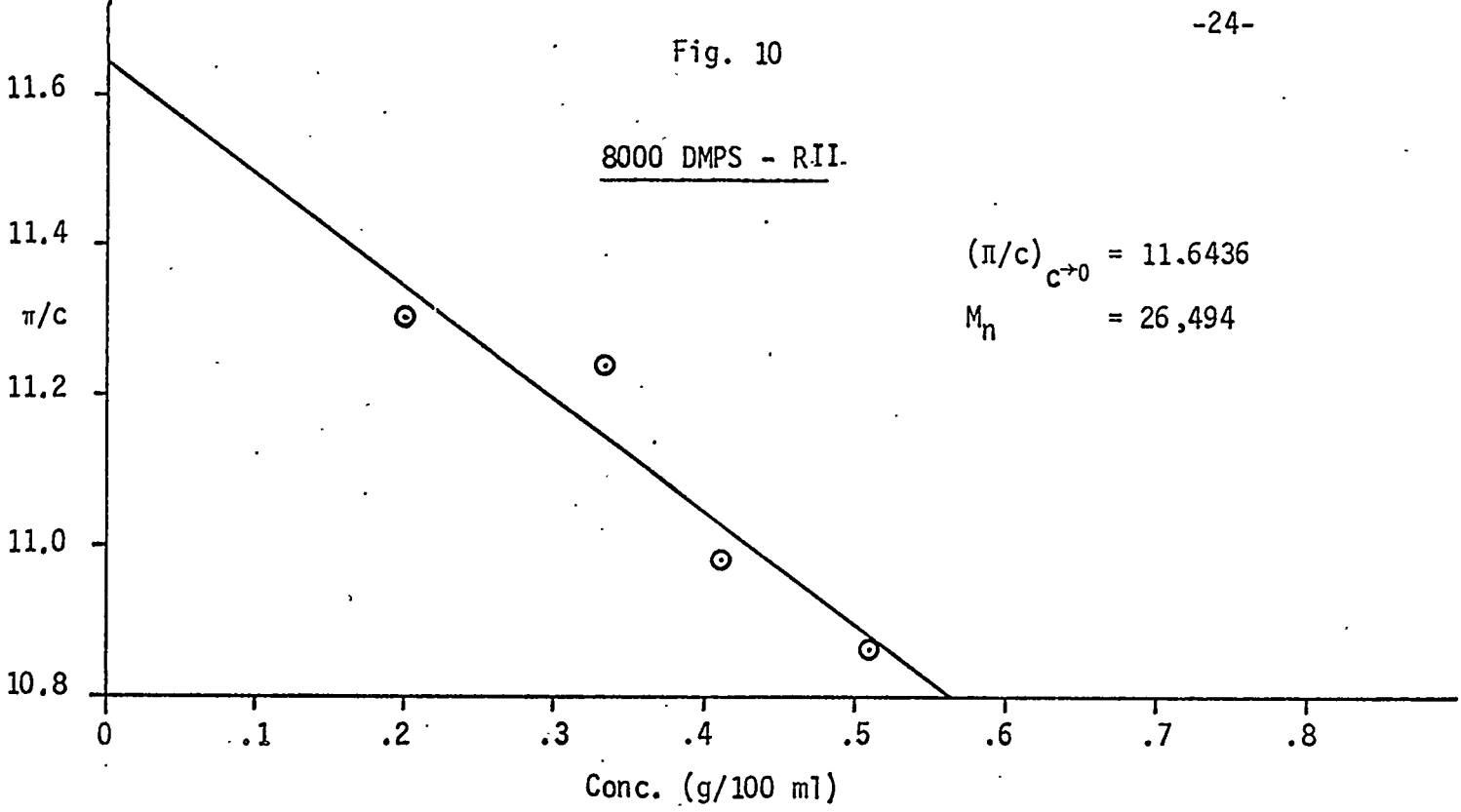


$(\pi/c)_{c\to 0}$ = 11.7209

M_n = 26,307

Fig. 10

8000 DMPS - RII

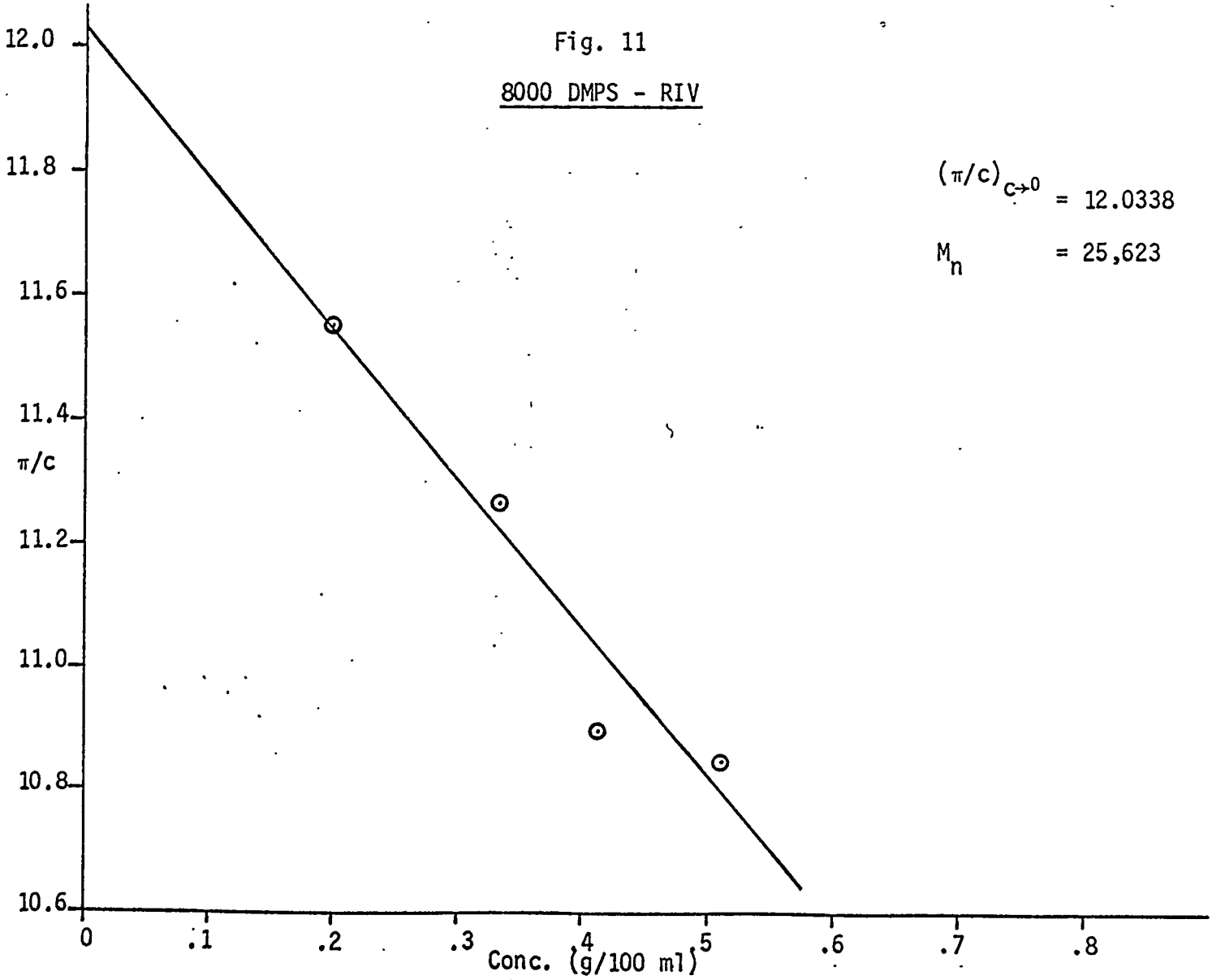


$(\pi/c)_{c\to 0}$ = 11.6436

M_n = 26,494

Fig. 11

8000 DMPS - RIV



$(\pi/c)_{c\to 0}$ = 12.0338

M_n = 25,623

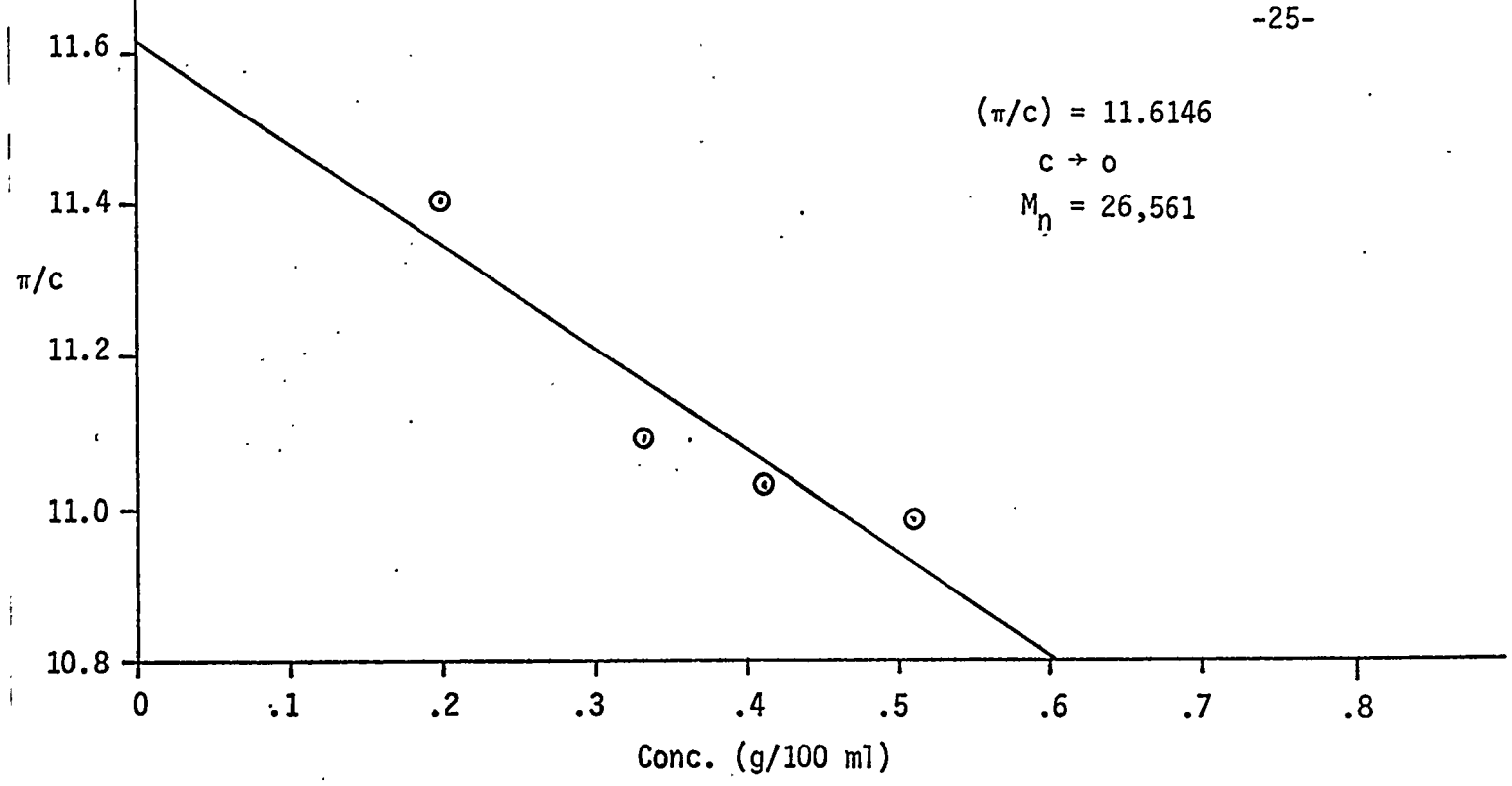


Fig. 12 8000 DMPS-RV

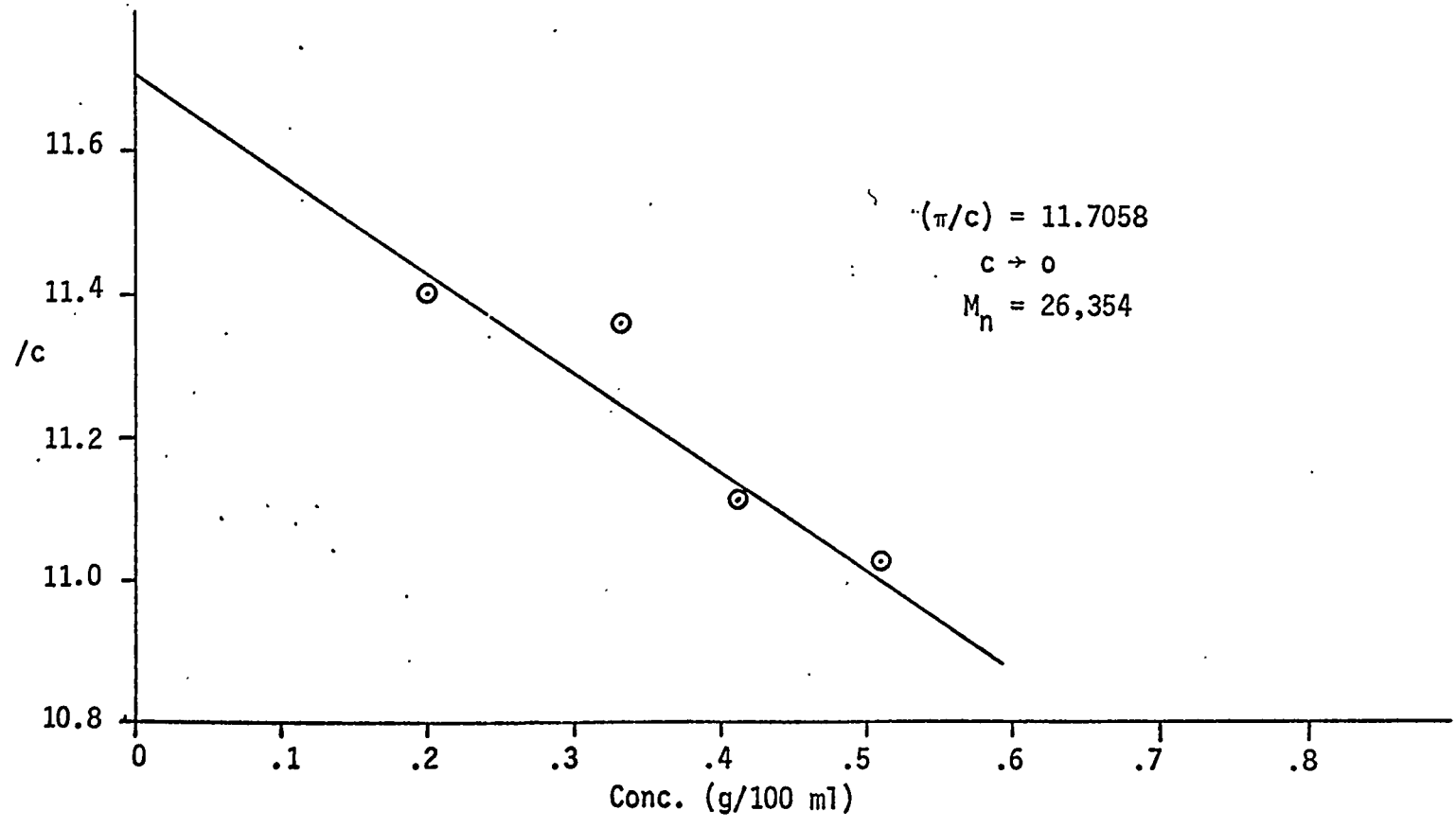


Fig. 13 8000 DMPS-RVI

Fig. 14 Composite Graph 2300 DMPS

Range = 3.700 - 3.875
M_n Range = 20,500 - 22,500
Midpt of Range = 21,500 ± 1000

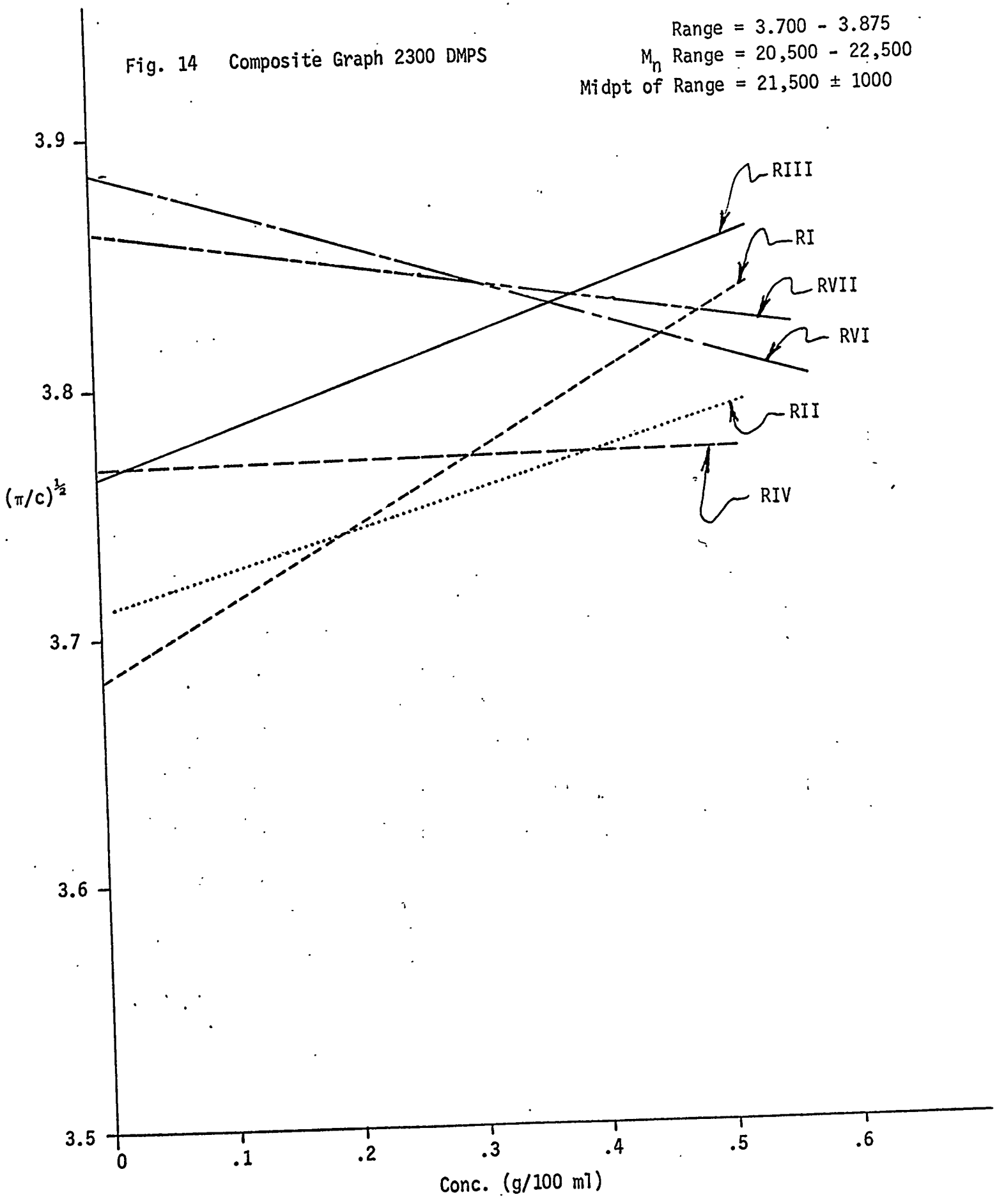


Fig. 15 Composite Graph 2300 DMPS

Range = 13.76 - 14.93

M_n Range = 20,662 - 22,419

Midpt of Range = 21,540 ± 880

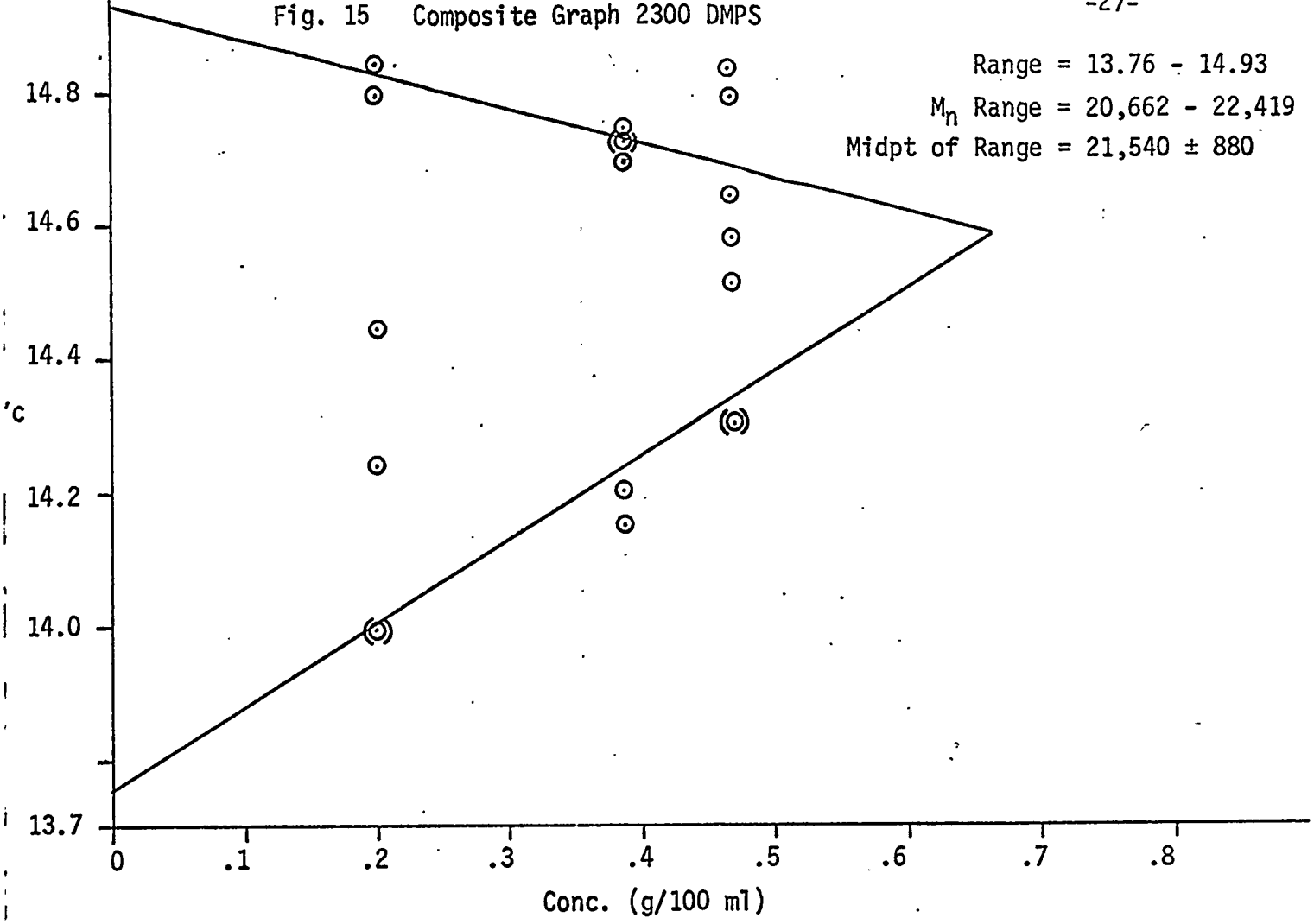
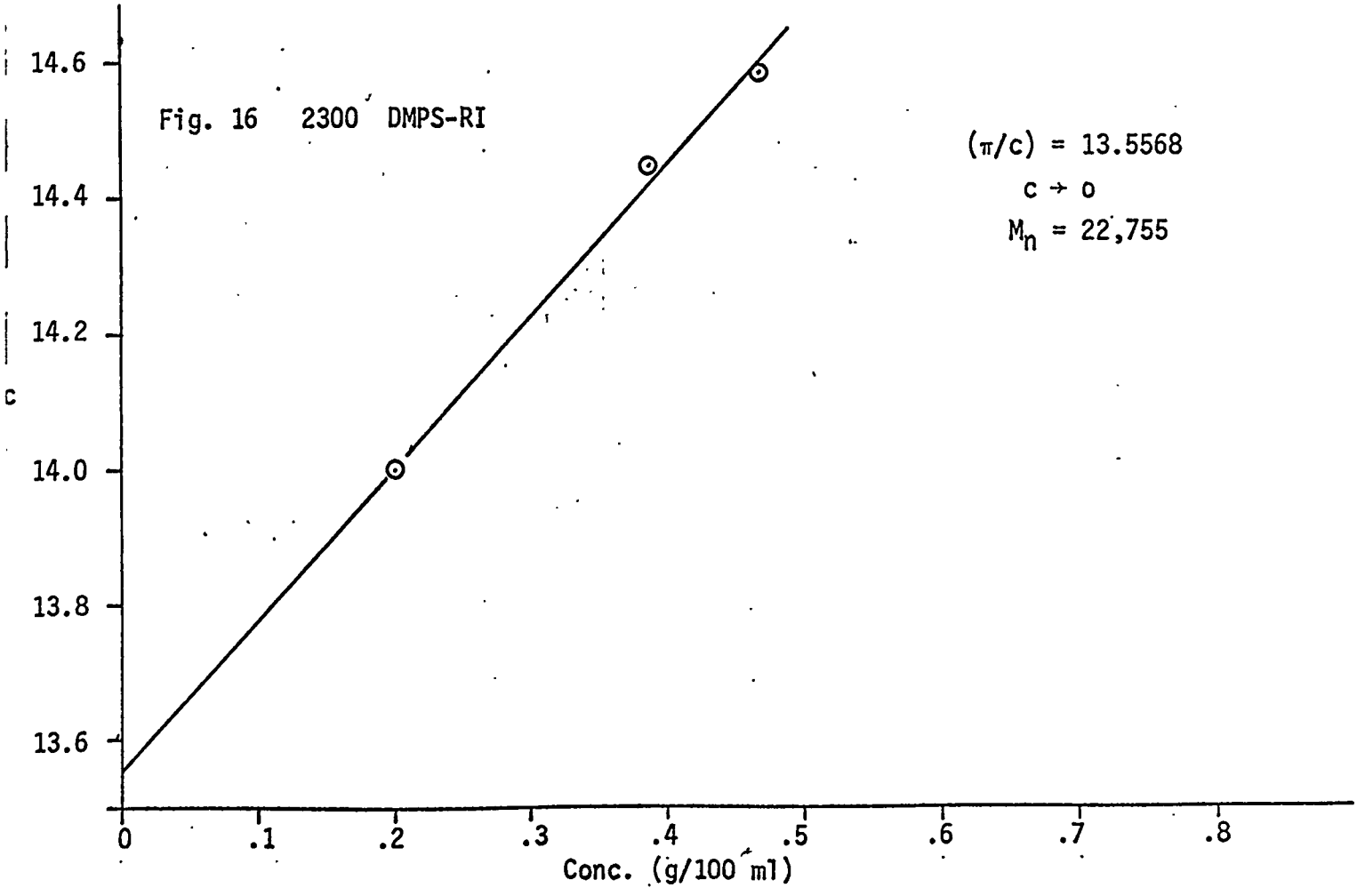


Fig. 16 2300 DMPS-RI

$(\pi/c) = 13.5568$

$c \rightarrow o$

$M_n = 22{,}755$



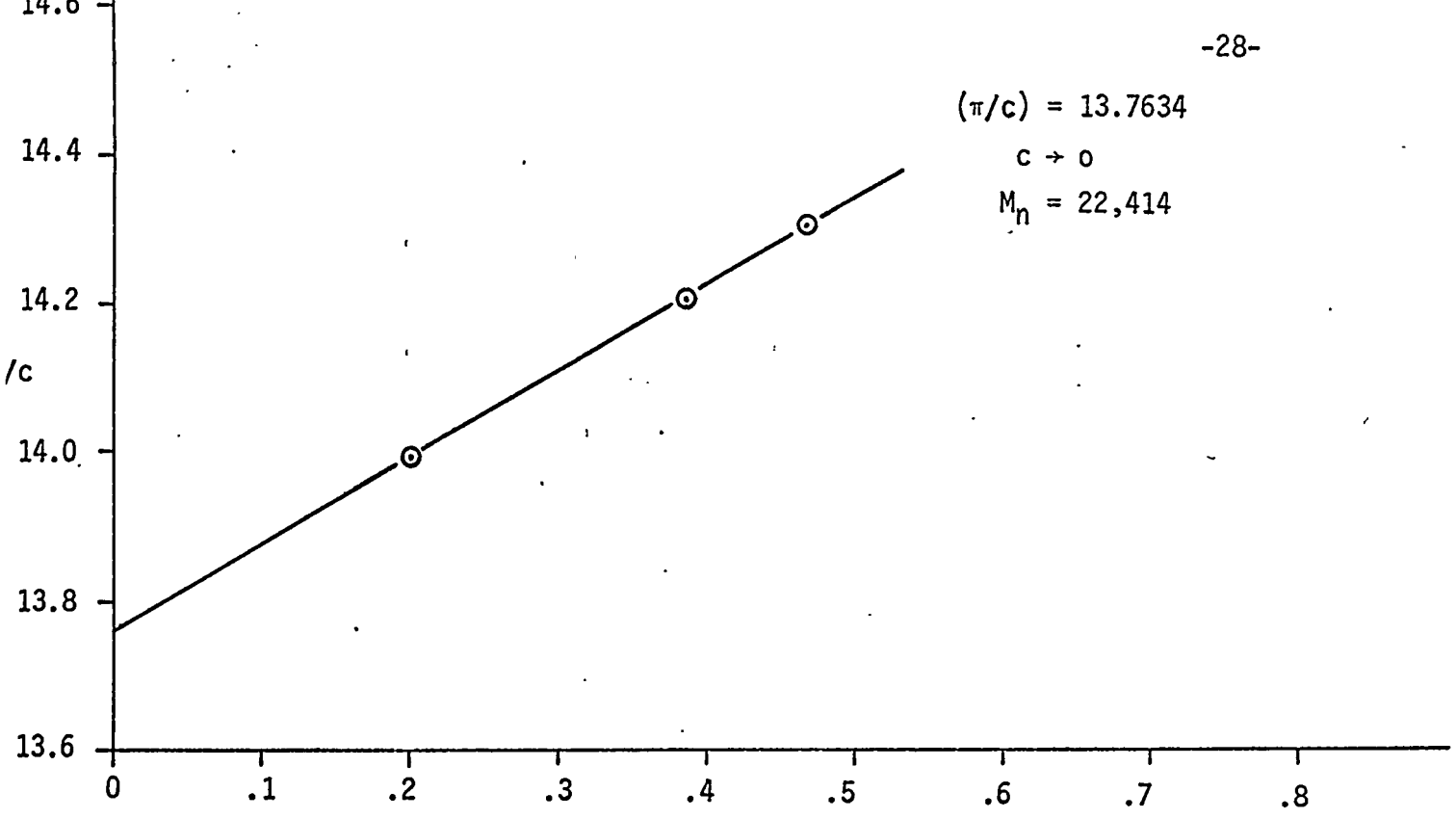


Fig. 17 2300 DMPS-RII

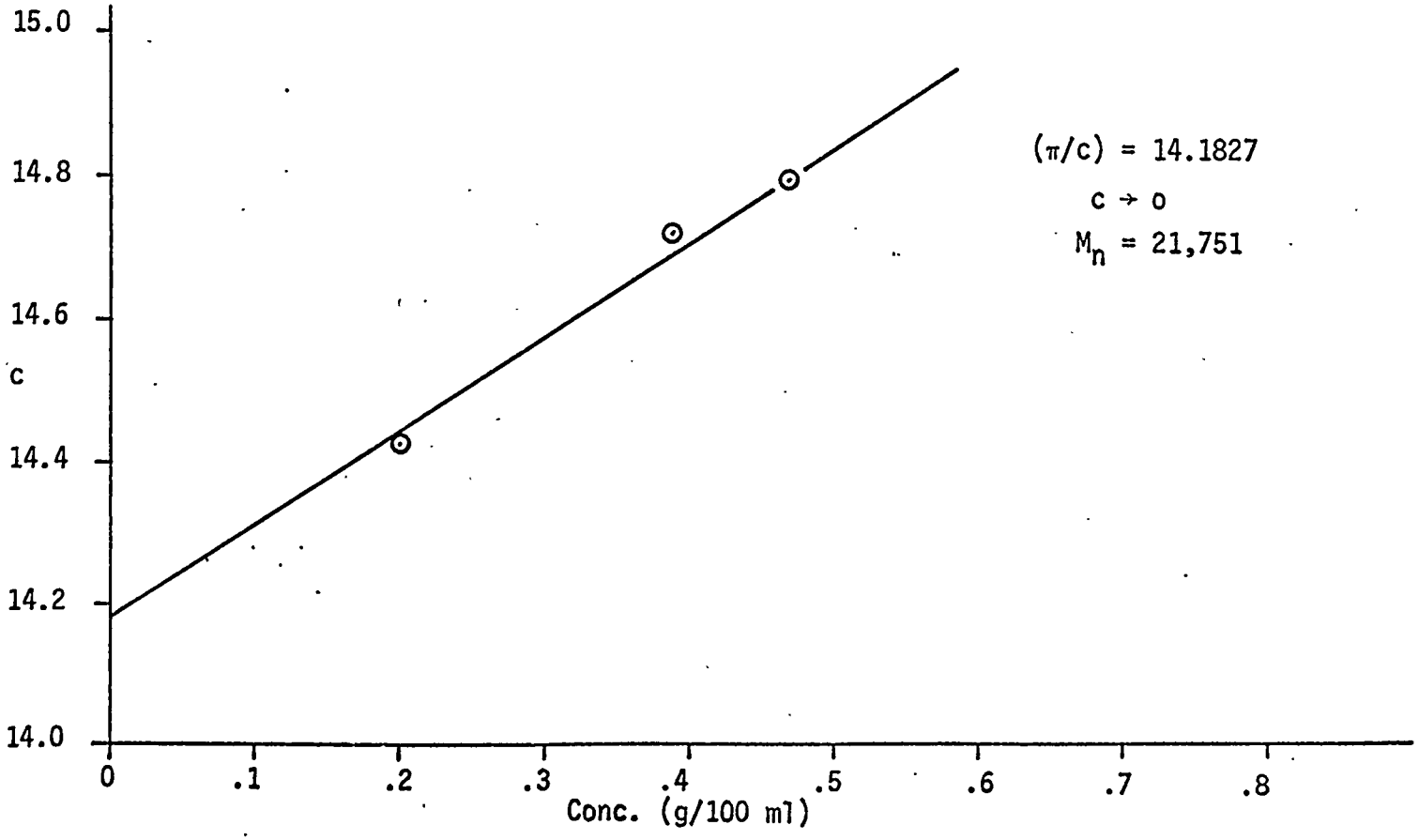


Fig. 18 2300 DMPS-RIII

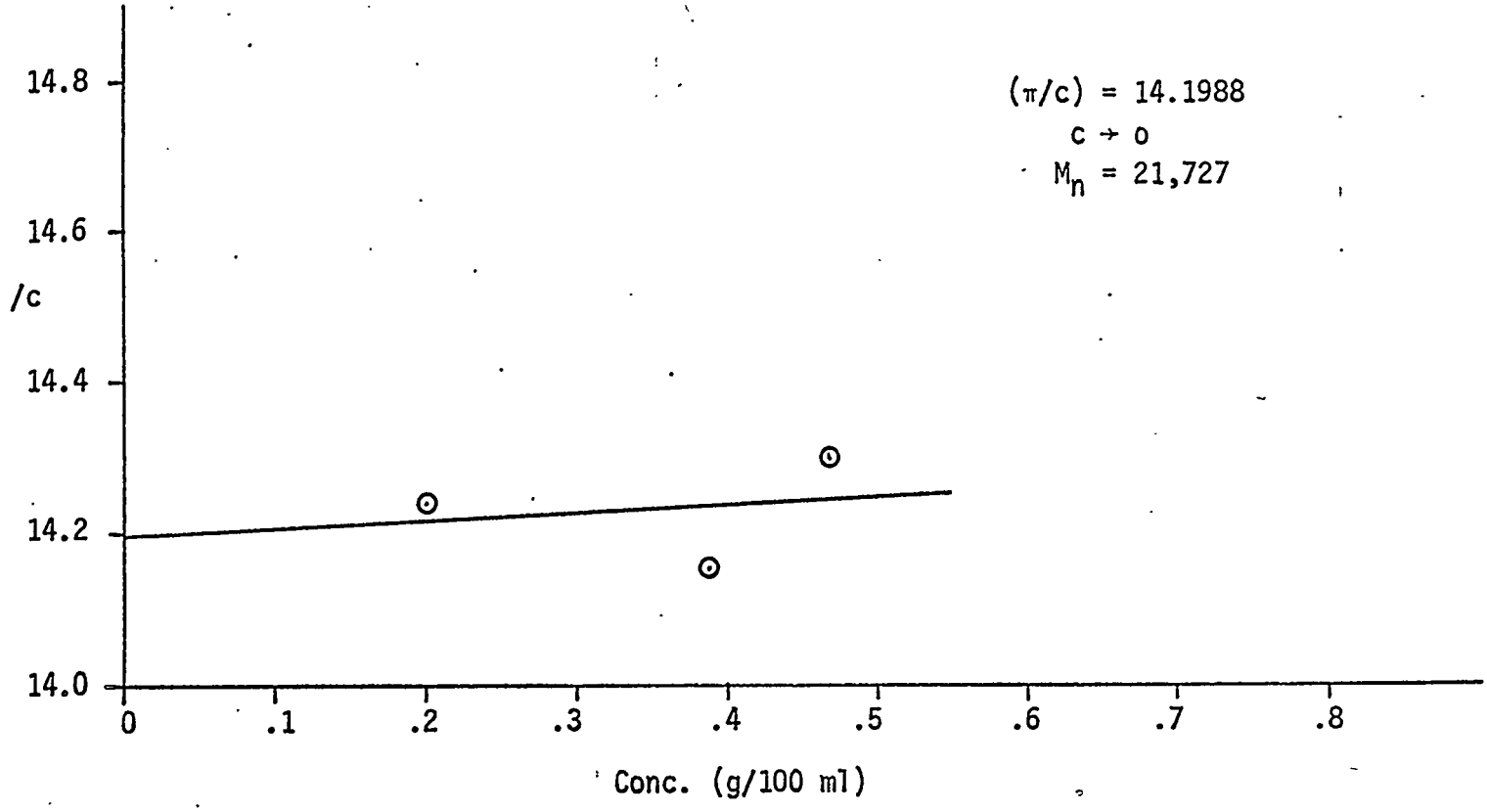


Fig. 19 2300 DMPS-RIV

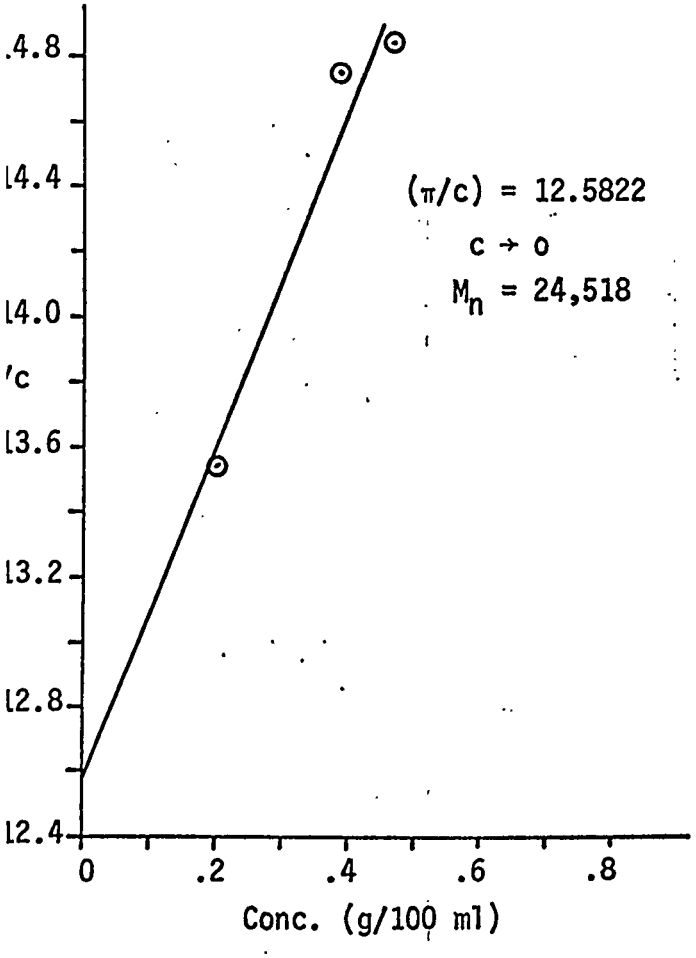


Fig. 20 2300 DMPS-RV

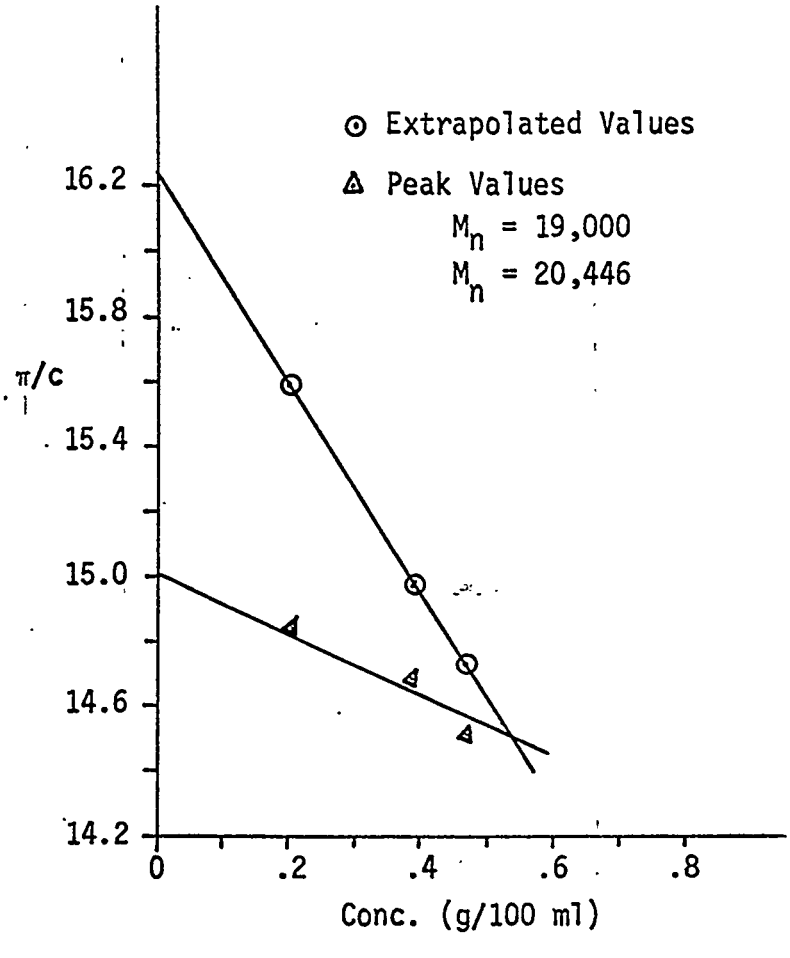
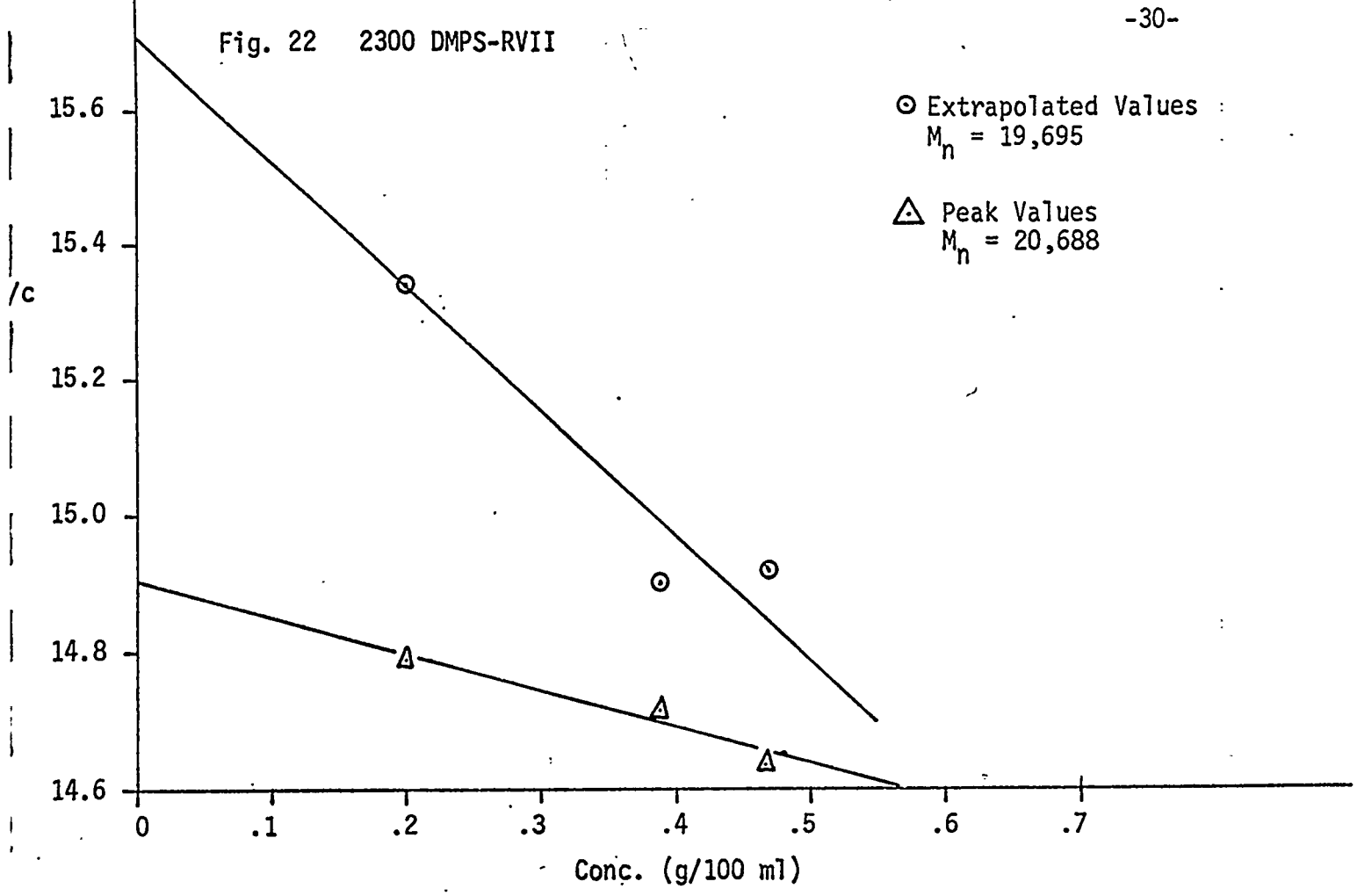


Fig. 21 2300 DMPS-RVI

Fig. 22 2300 DMPS-RVII



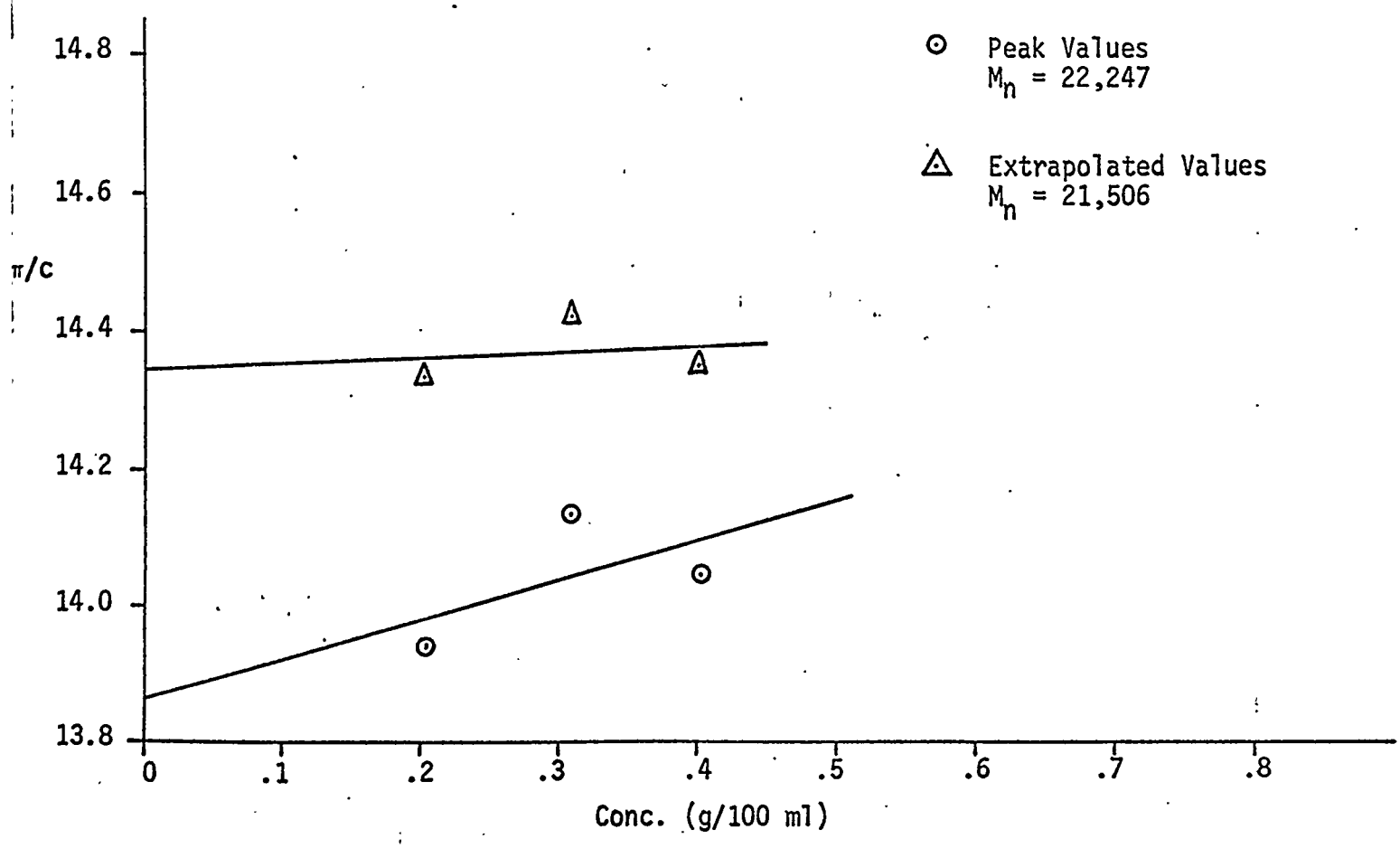


Fig. 23 Mixture #1 DMPS-RIII

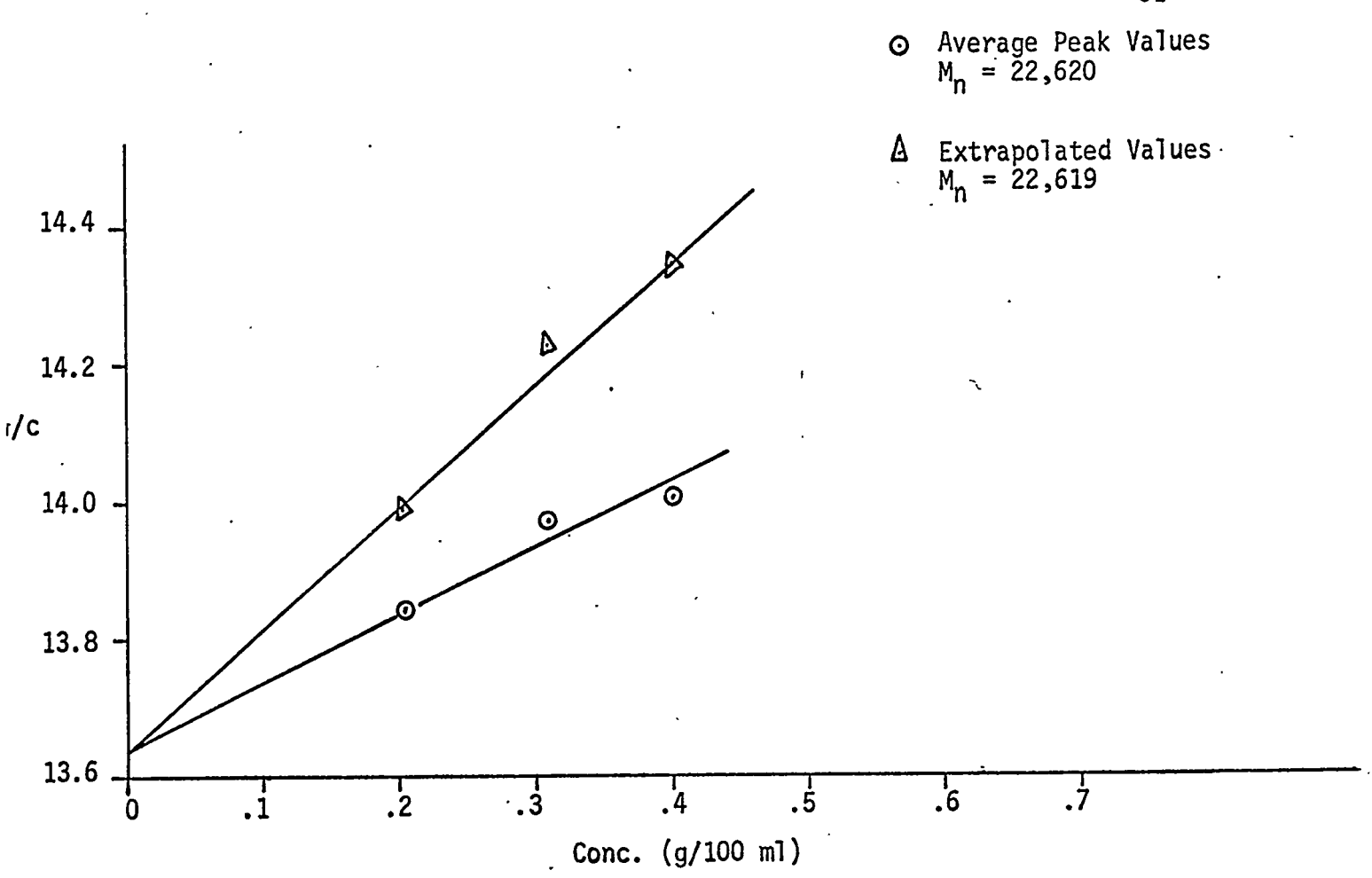


Fig. 24 Mixture #1 DMPS-RII

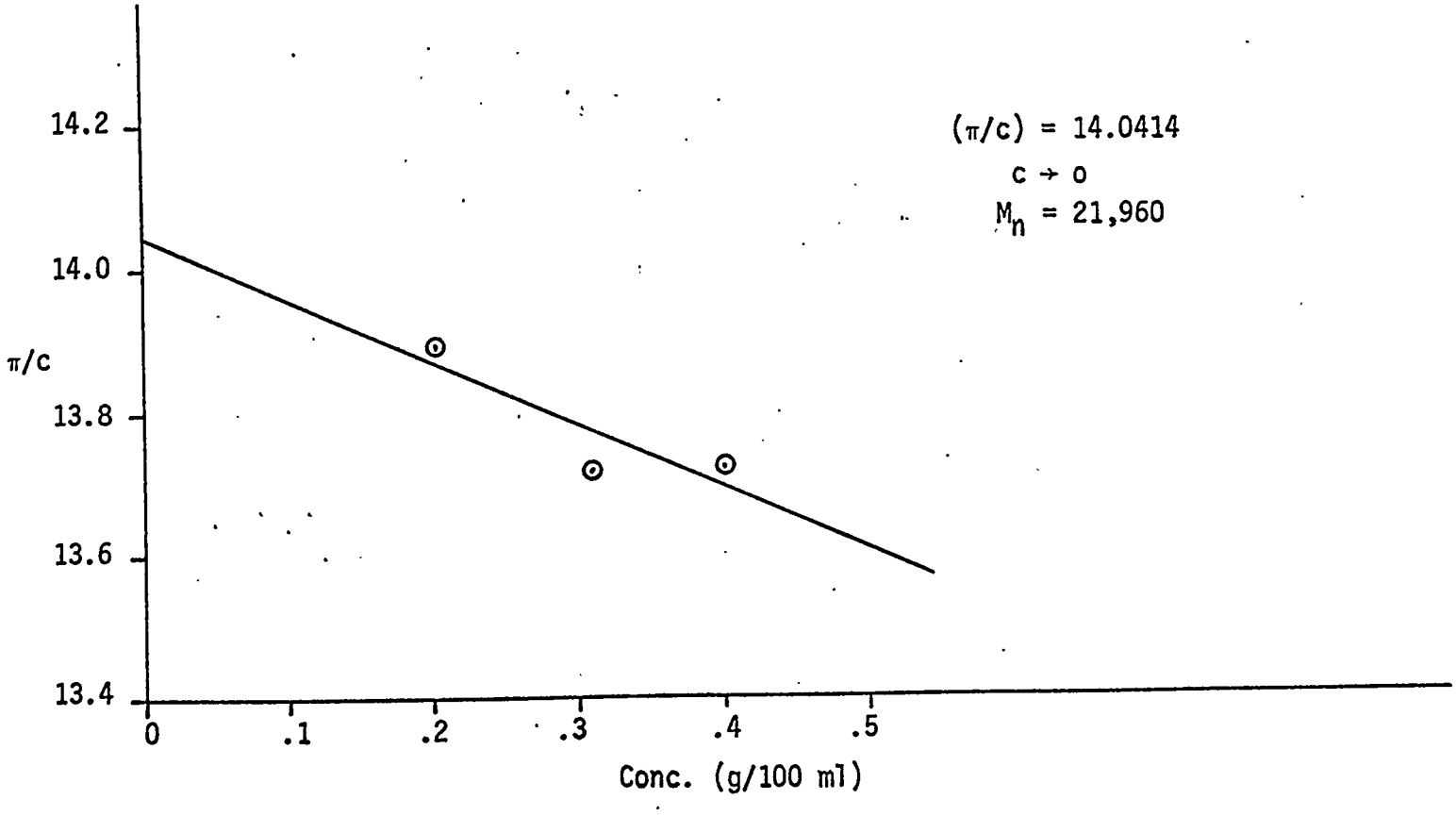


Fig. 25 Mixture #1 DMPS-RI

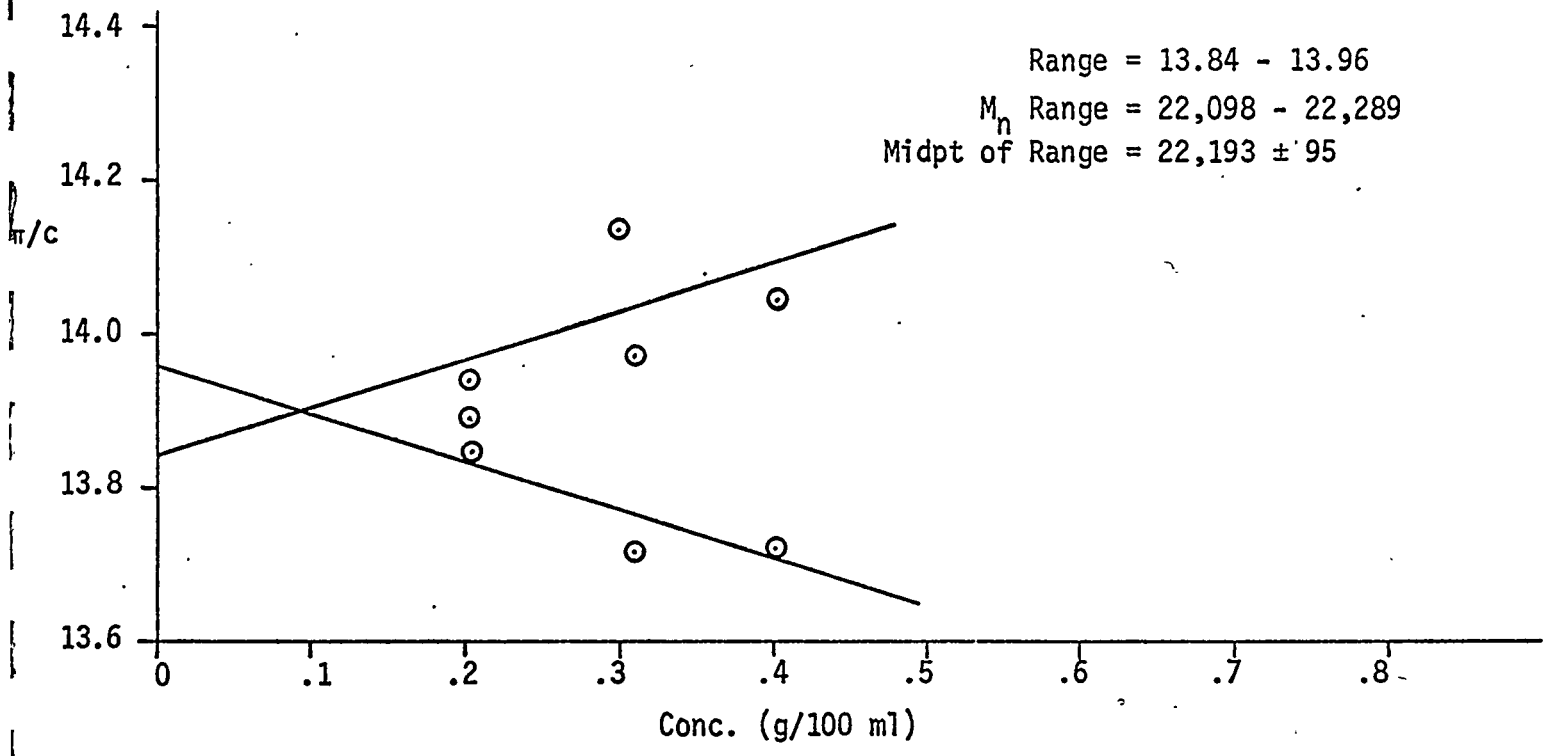


Fig. 26 Composite Graph Mixture #1

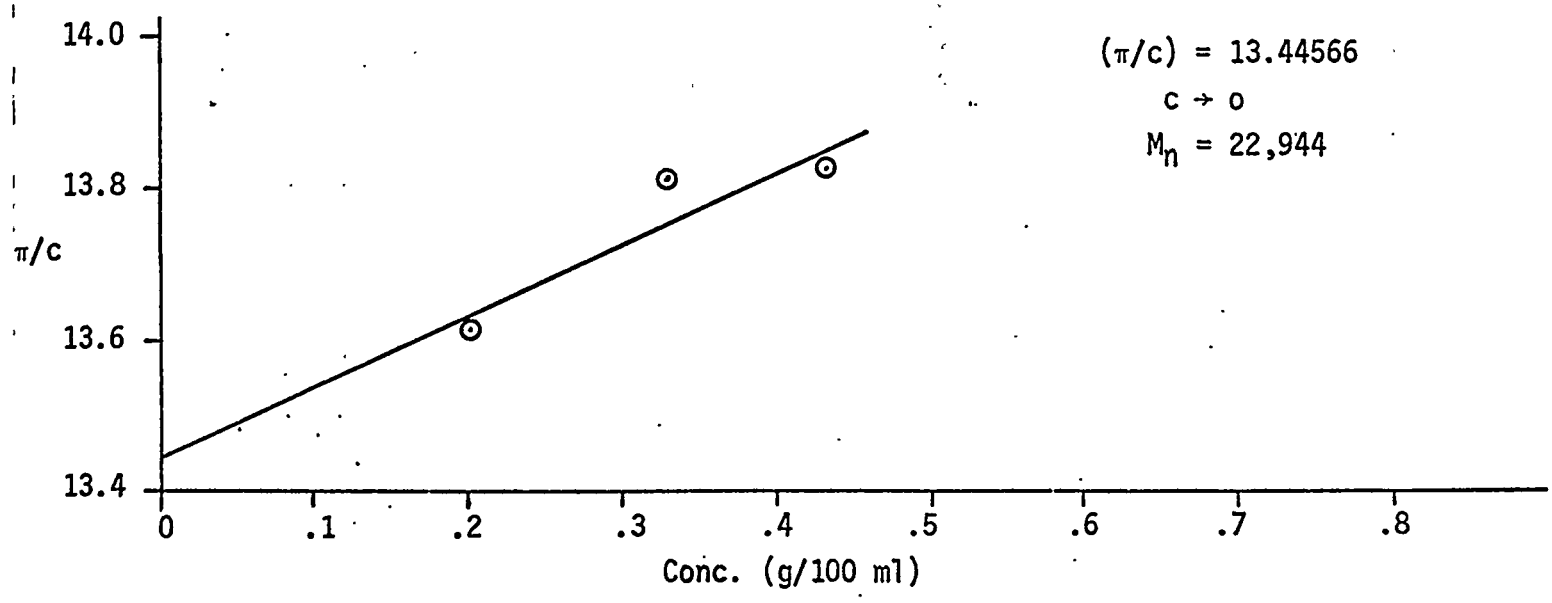


Fig. 27 Mixture #2 DMPS-RI

Fig. 29 Mixture #2 DMPS-RIII

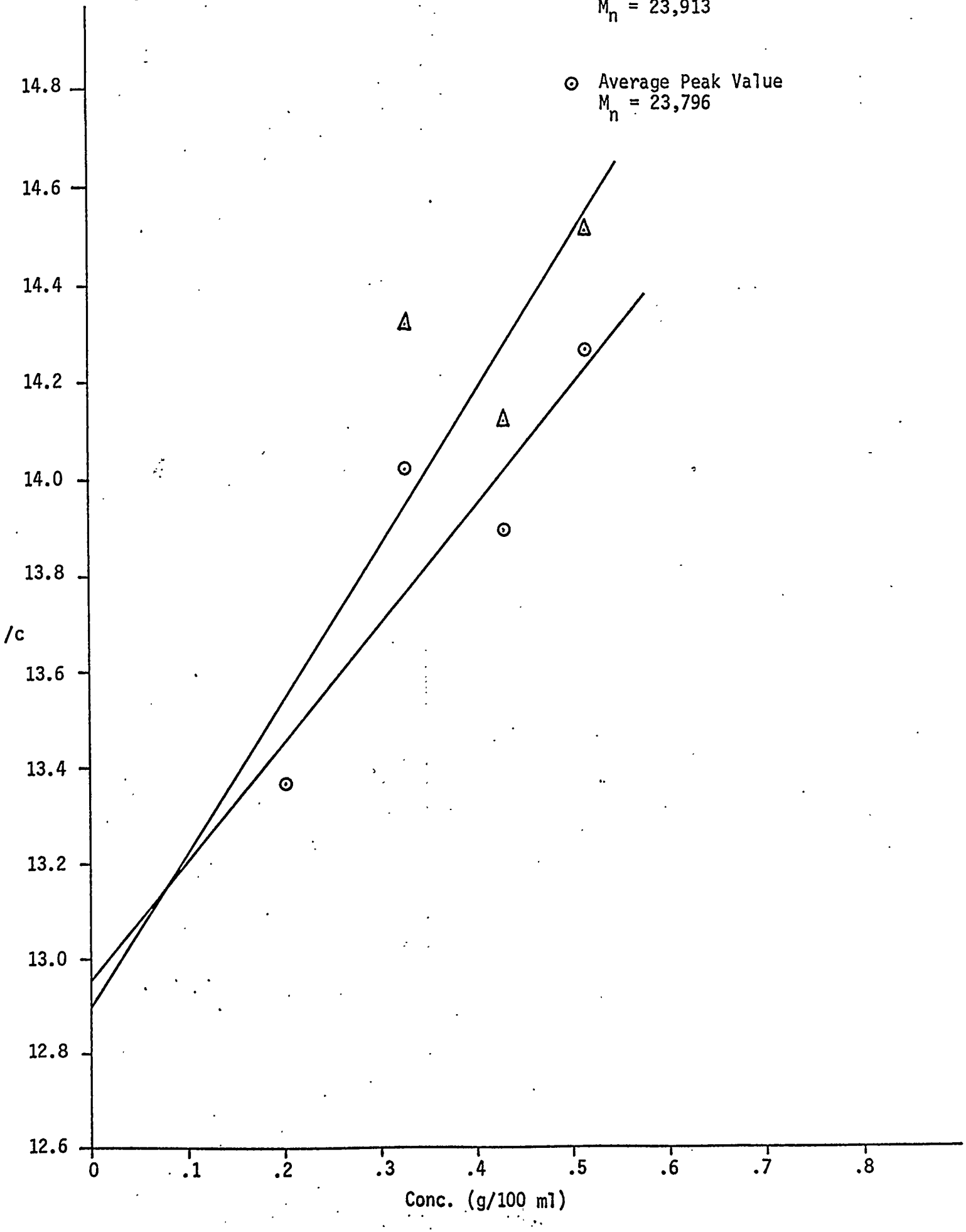


Fig. 30 Composite Graph Mixture #2

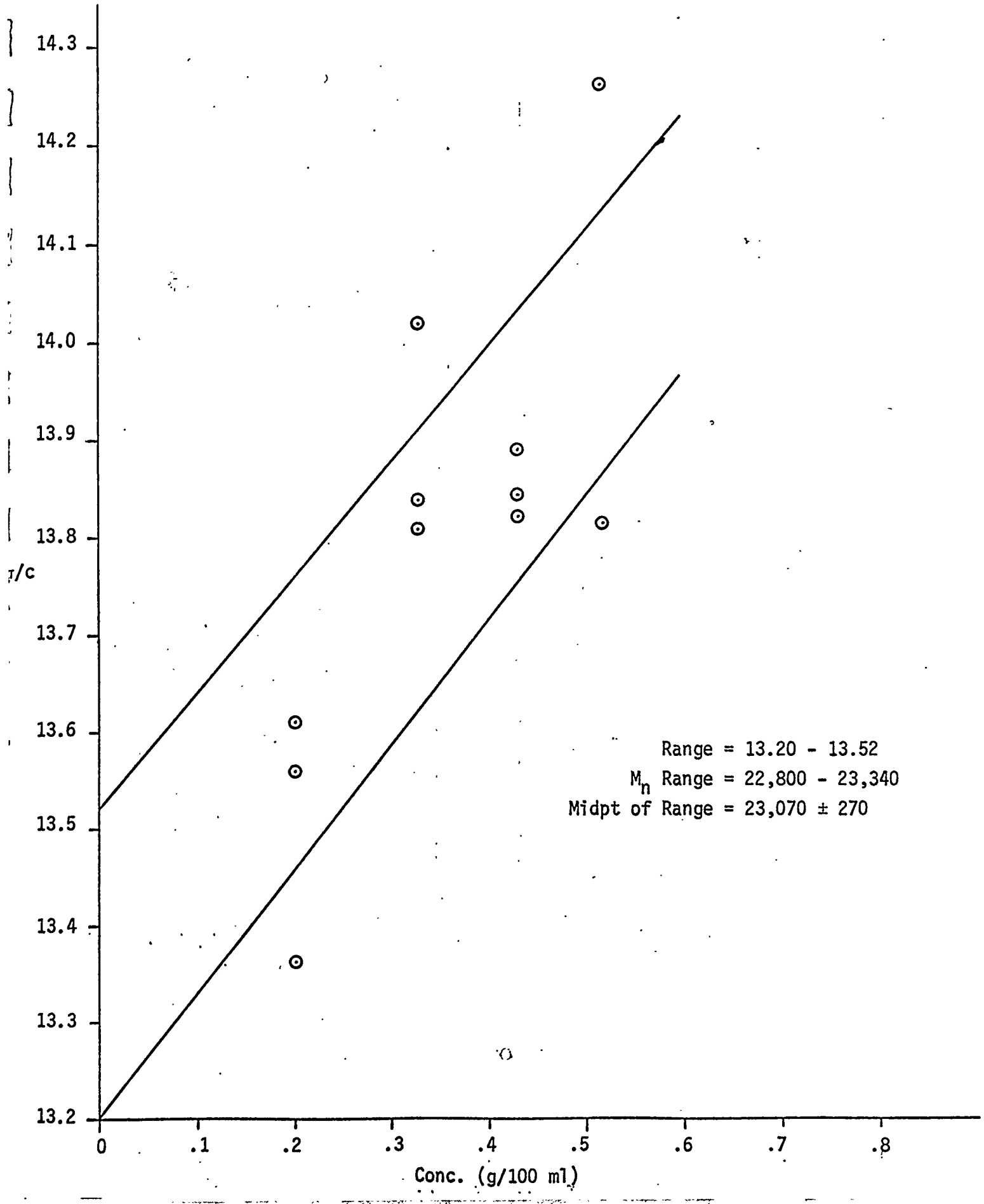


Fig. 33 Mixture #3 DMPS-RIII

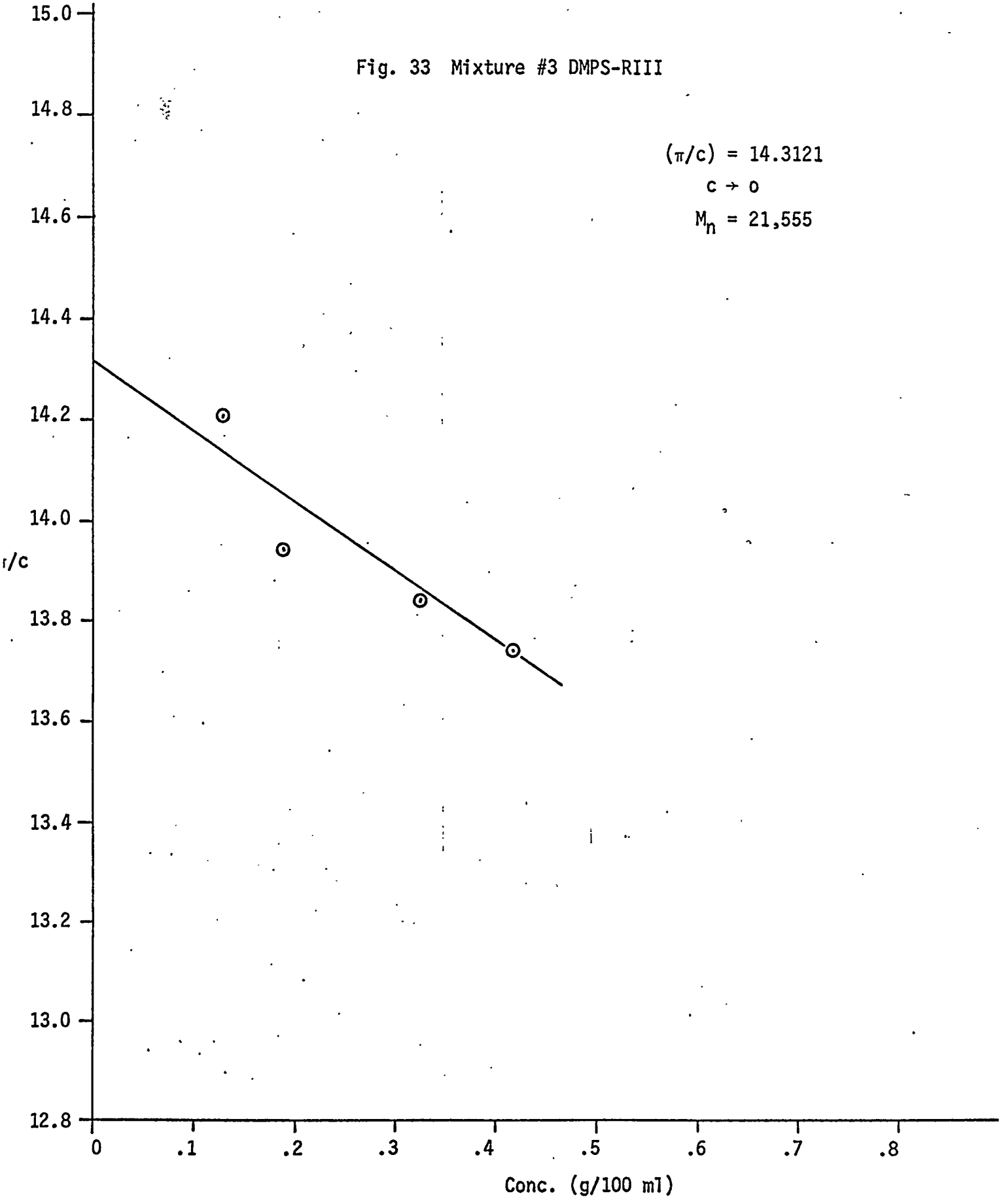


Fig. 34 Composite Graph Mixture #3

Range = 13.90 - 14.34

M_n Range = 21,500 - 22,150

Midpt of Range = 21,825 ± 325

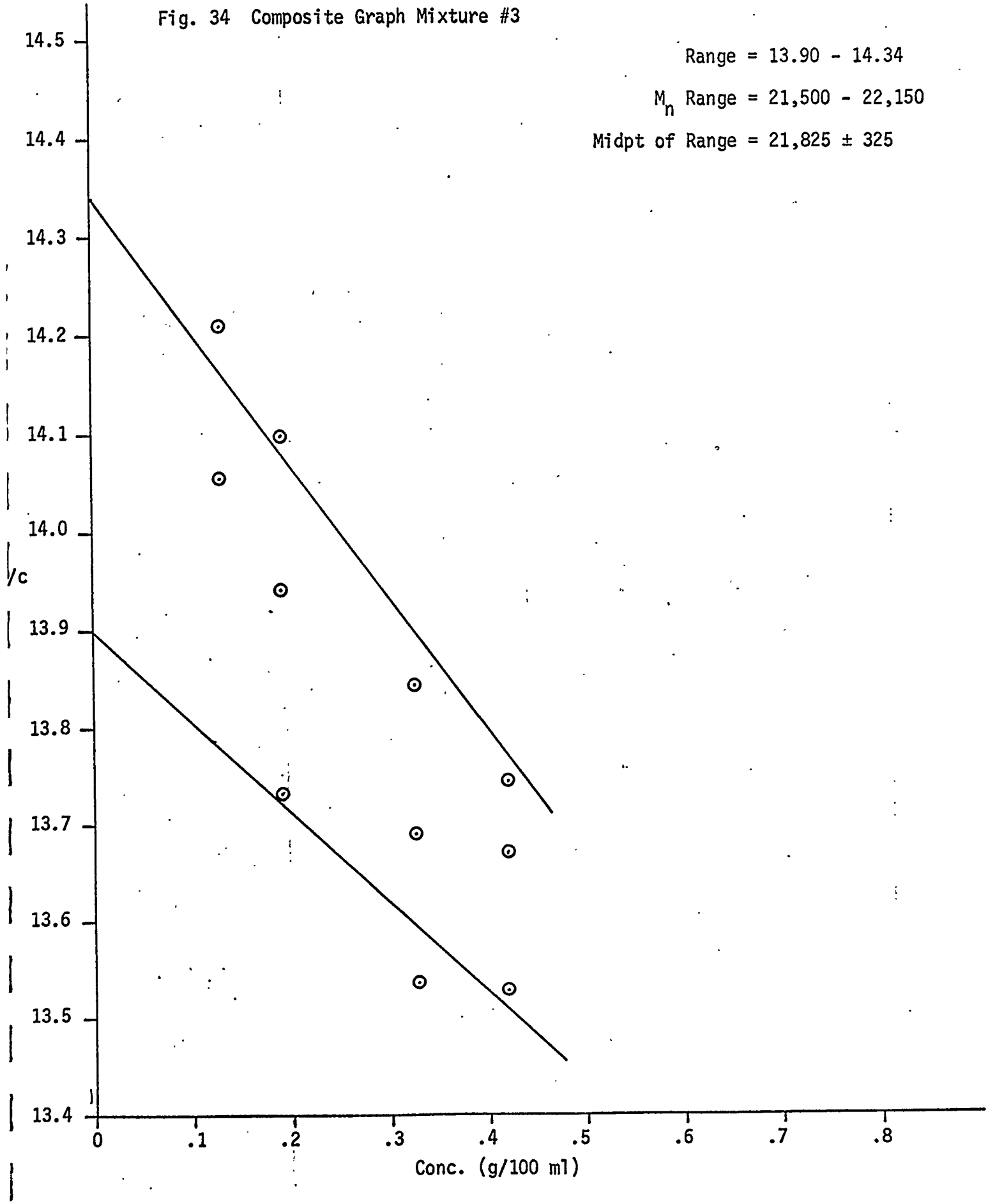


Fig. 35 Mixture #4 DMPS-RI

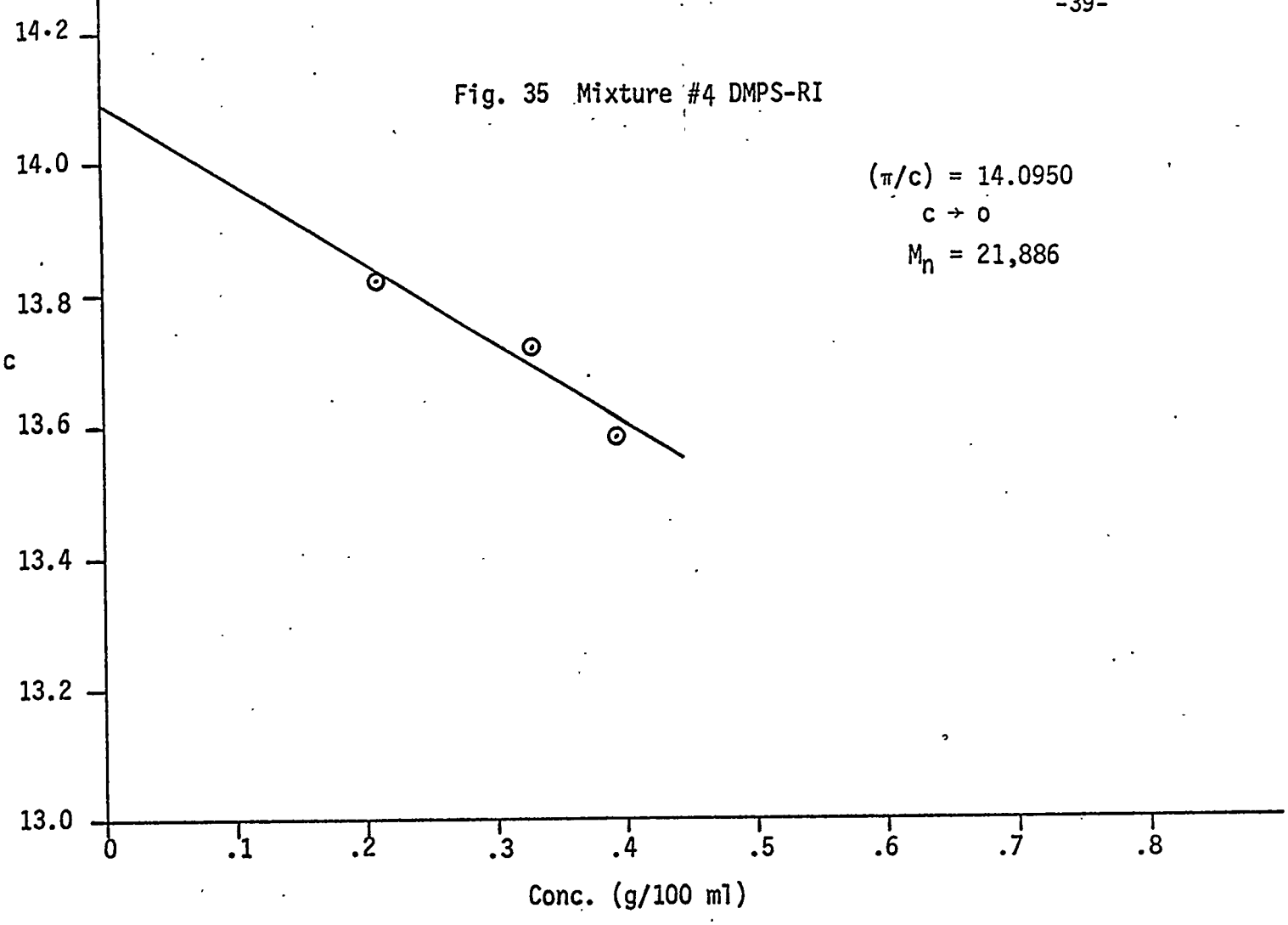
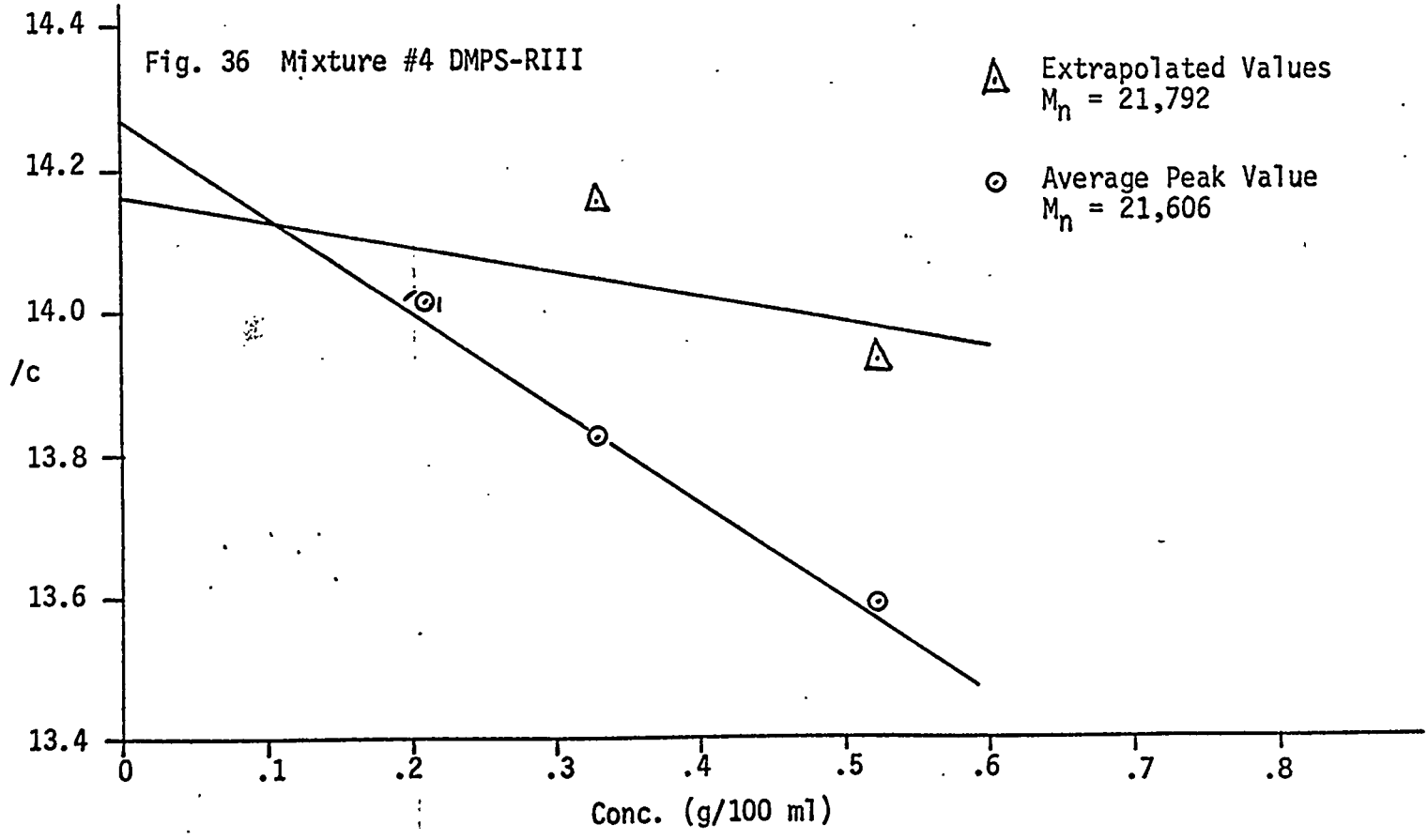


Fig. 36 Mixture #4 DMPS-RIII



CONCLUSIONS: EVALUATION & SUGGESTIONS

The eventual use of the number-average molecular weight (M_n) with the weight average molecular weight (M_w), or some property related to M_w (e.g. viscosity) as a method of characterizing the molecular weight distribution of the silicone polymers is a future goal. Knowledge of the distribution, without running a gel permeation chromatogram, is preferable to maintain meaningful specifications on the polymers. If the variations in curing results are ever to be eliminated, changes in the molecular weight distribution of the elastomers from lot-to-lot will also have to be eliminated. The number average molecular weight (M_n) alone cannot characterize the distribution. In fact there is no relation between M_n and the distribution curve. However, the gross features, namely the peak and the breadth, can be approximated when both M_n are known. The ratio M_w/M_n equals the breadth. It is indicative of the breadth only when the ratio is less than 4 and M_n is known with certainty.

Therefore, the problem is whether M_n can be accurately measured with the methods available, namely the membrane osmometer. From the results, the answer is no. The author realizes that the membrane used 600 gel cellophane while being retentive to particles of molecular weight greater than 7000, is not completely compatible with the Shell Hallikainen automatic osmometer - in that it causes some oscillations of the servo (recorder) mechanism. However, from tests previously conducted by Melvin Friday under Garland Barnes, a former Pantex associate, this oscillation was so slight that it did not affect the accuracy of the readings. Yet upon examination of my recordings of a typical run, small, but noticeable blips

are present. Perhaps the blips were caused by surges in the line voltage (a voltage regulator has been ordered) or some malfunction of the machine. As stated in the section marked "troubles" attempts were made to discover and correct these oscillations, but to no avail. Time is a great disadvantage of this method. To conduct a run on 3 - 4 concentrates and establish a reproducible baseline, at least 2½ hours are required, if all is functioning correctly. Any repairs to the instrument which require removal of the outer shield destroys the thermal equilibrium. Depending on how far the temperature drops - the system will require 3 - 4 hours to reach equilibrium. If the membrane is changed, usually it will be two days before the membrane is conditioned and the temperature is stable. Since the emphasis was placed on obtaining the data as readily as possible, the problem was alleviated, but not completely removed.

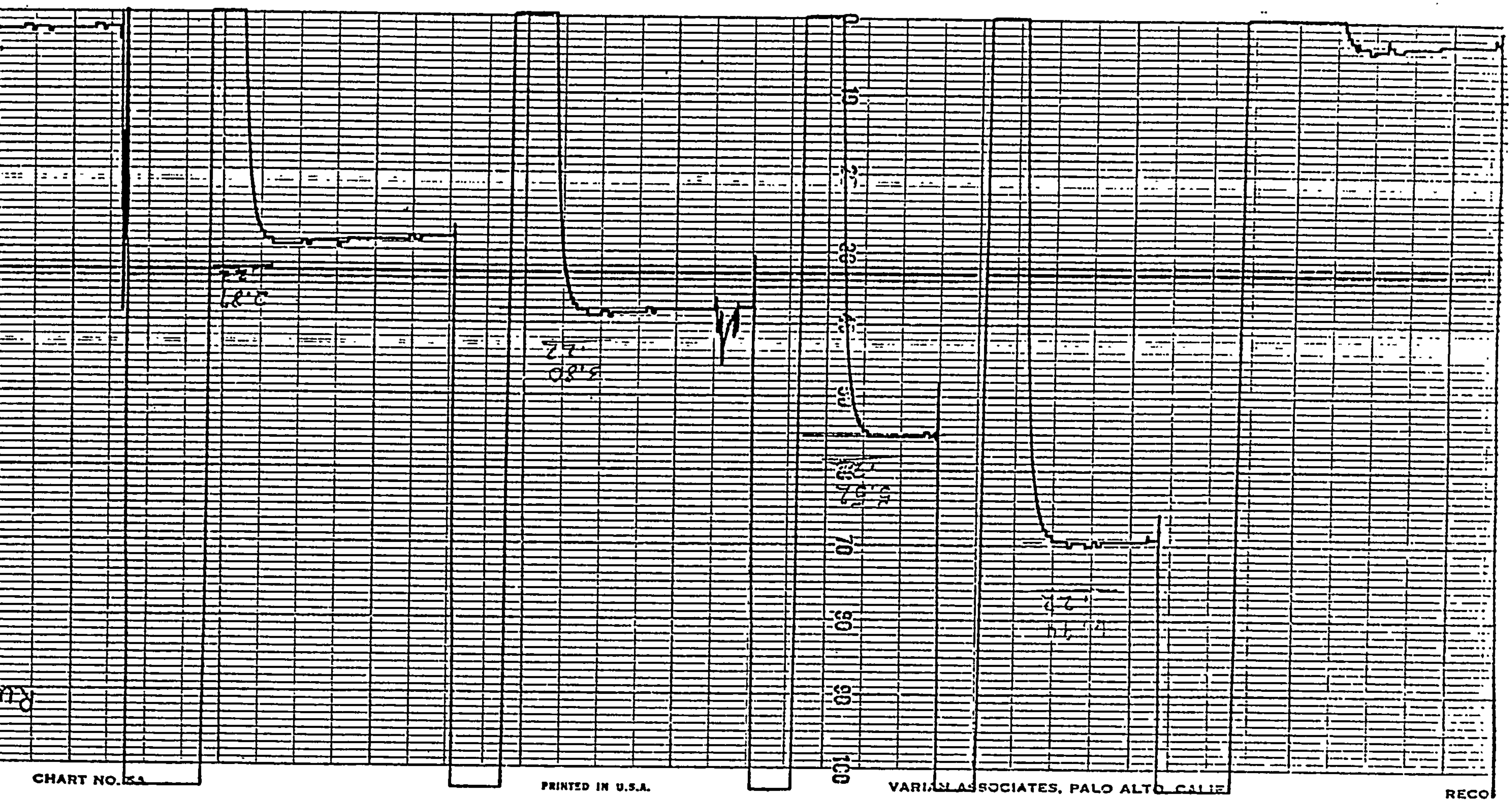
So the question is whether these oscillations were the main reason for the negative reply earlier. Obviously again no!! My decisions are based on the following arguments:

(1) Even when smooth curves are obtained, the readings depend too much on personal interpretations. A value calculated from any graph has an uncertainty of ± 3 - 5%.

(2) The instrument is too insensitive to slight changes in distribution. From the molecular weights of the mixtures of 2300/8000 it was impossible to determine a trend of increasing molecular weight and little less related the numbers back to the ratio of 2300/8000 in the mixture.

(3) Time is a major disadvantage. Two and a half hours are required for one run. If the solute permeation is appreciable, a baseline

0
10
20
30
40
50
60
70
80
90
100
RECORDER DIVISION
VARIAN ASSOCIATES, PALO ALTO, CALIF.



10
20
30
40
50
60
70
80
90
100
CHART NO.
PRINTED IN U.S.A.
ASSOCIATES, PALO ALTO
RECO

has to be established after concentration, so only one run could be made in a day. One usually figures at least 6 - 8 runs would constitute an acceptable population; therefore, a week would pass before a value for M_n could be given.

(4) Neither Arro's 600 gel cellophane or the S & S-B-20 membranes are ideal semi-permeable membranes (only the solvent and molecules pass through). They are both permeable to species of low molecular weights (< 7000). If they were not, hours would pass before the osmotic pressure attained an equilibrium value. According to Staverman who treated this defect theoretically, "osmotic experiments only yield true number average molecular weights when no solute permeates the membrane. In fact the molecular weight obtained counts the larger molecules more than the smaller ones--- Finally we concluded that in all cases where appreciable leakage occurs in dynamic measurements, very little can be shown"[5].

Theory and experiment show that the apparent osmotic pressure when leakage occurs is always less than the true value. Even extrapolation back to time of final closure of outlet valve does not correct for the solute permeation.

Finally from the experiences of past work conducted by Garland Barnes, I do not think that changing the membrane and increasing the number of runs on a sample will ever provide the degree of reproducibility desired (a variance of ± 1% would be necessary when we are missing two samples

[5]*A. J. Staverman, Rescueil des Travaux Chemie, 70, 351 (1951).*

E. Small amounts of samples are needed (< 3 ml.).

F. As the fractions come off the column they can be collected and further analyzed (i.e. analyze the low molecular weight samples to determine whether they are cyclic or straight chains).

Some of the disadvantages are the following:

A. GPC is new and thus has not completely proven itself. Samples have been submitted to four different analyzing services that use GPC methods. The results should determine its merit.

B. Since GPC is new, little information has been accumulated concerning its sensitivity to a slight shift in distribution. I would suggest the mixtures of 2300/8000 also be analyzed.

C. In talks with Sliemer of Battelle, he admitted that resolution of the low molecular weights molecules needed improvement - otherwise the M_n was too uncertain. He felt confident that the inclusion of another column would eventually correct this defect.

APPENDIX

TABLE OF CONTENTS

VAPOR PHASE OSMOMETER PROCEDURE

The procedure followed is based on the one given in Mechrolab's Operation Manual. Helpful details have been added.

I. Initial Check-in.

A. Check connection to battery and condition of fuse.

B. Fill vapor heat chamber to the bottom of the circle on the wick with the solvent to be used.

C. Replace upper case and allow 4 - 5 hours for temperature to equilibrate.

D. Turn on Null detector.

E. Prepare solutions with concentrates between 0.005 molar - 0.1 molar.

F. After thoroughly cleaning the syringes and rinsing with solvent, fill the first four with samples, arrange in order of increasing concentration.

II. Temperature Stability Check.

A. Rinse the thermistor beads with 8 drops of pure solvent from syringes #5 and #6. Then place a solvent drop of equal size on each bead.

B. Turn Bridge on-off switch to on and the ΔR-R switch to test position.

C. Depress the zero button and center needle with zero control.

D. Wait 30 seconds then rotate the T potentiometer until the needle is near the center of the scale (potentiometer should read approximately 440). The potentiometer is too sensitive to allow exact centering of the needle. Therefore, adjust it

4. Wait exactly 30 seconds then adjust the ΔR dials until the needle is centered. If the needle drifts, readjust ΔR dials. The final reading is taken after 2 minutes have elapsed from applying the sample drop.
5. For an unknown solute, ΔR readings should be taken after 2, 3 and 4 minutes.
6. Repeat steps 1 - 5 by adding a new drop to the sample bead (no rinse is needed).
7. Proceed to syringes 2, 3, & 4. Repeat steps 1 - 6 for each concentration.
8. After completion of a series, rinse the sample bead with 20 drops of solvent from syringe 5, and recheck the zero point. The needle should be within the V at the center. If it lies to the (-) side, rinse the sample thermistor again. If it lies to the (+) side, the reference drop has been contaminated. For the polymer solutions, the reference drop had to be replaced each time a new solution drop was placed on the sample thermistor bead.
9. Remove upper case on thermal chamber, empty the liquid in the cup, and refill with fresh solvent.
10. Empty the syringes and rinse thoroughly with solvent. Do not store solutions in the syringes over night.

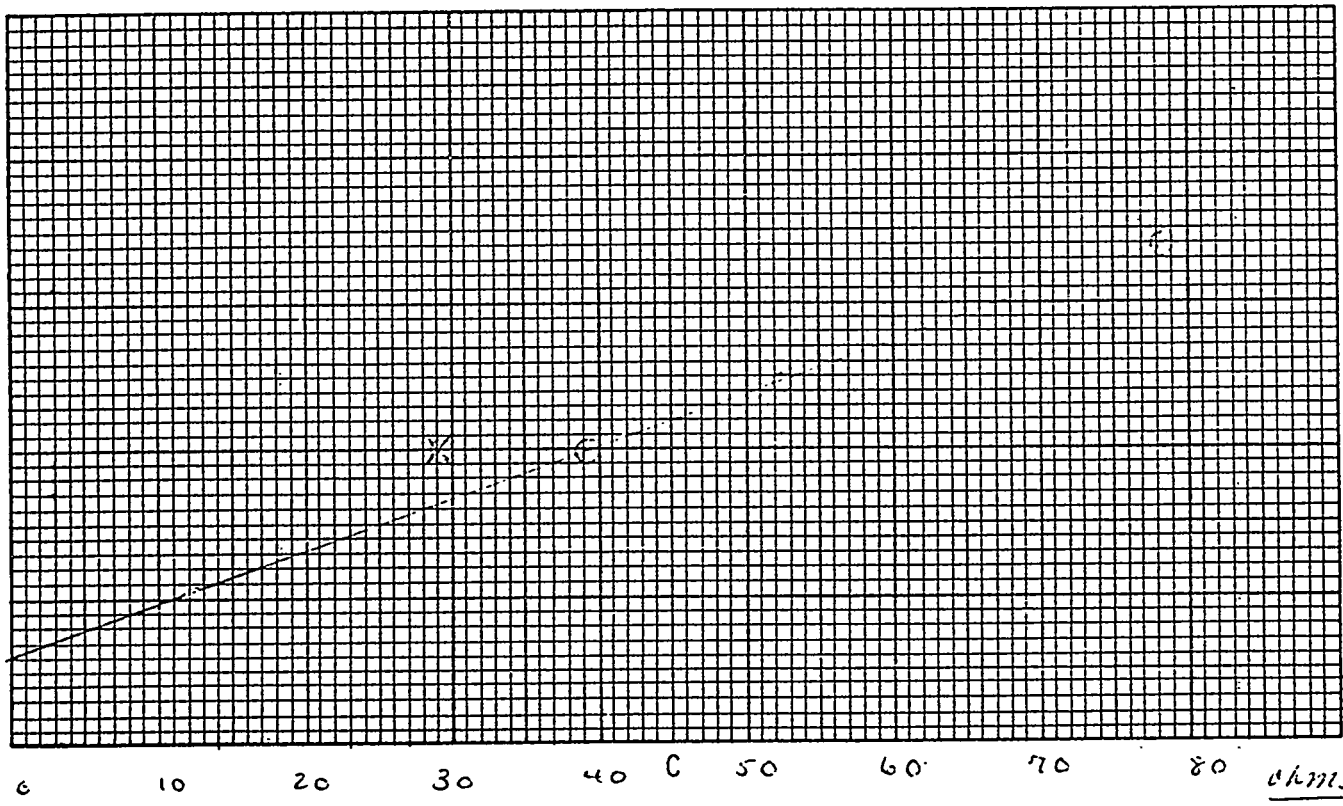
VAPOR PRESSURE OSMOMETERS WORK SHEET

Sample Polystyrene Standard Solvent Toluene | M_n =

Temperature ~~Room~~ 37° C. Probe No. _____ Instrument VPO

Calibration Standard 10,900 ± 5% = M_N Time Interval 2 min

						Remarks
Concentration, C	39.1296	58.6163	78.2593			
ΔR	1.58	2.23	3.66			
ΔR	1.55	2.23	3.68			
ΔR						
Average ΔR	1.565	2.23	3.67			
ΔR/C × 10^2	3.99953	4.23293	4.68954			



$(\Delta R/C)_{C \to 0}$ from graph 0.033100 69 Calibration Factor K = 360.80 ohms-10c g/mole

Molecular Weight = $\frac{K}{(\Delta R/C)_{C \to 0}}$ = _____ = _____

Analyst: J Lackey Date 7/11/68 No: _____

VAPOR PRESSURE OSMOMETERS WORK SHEET

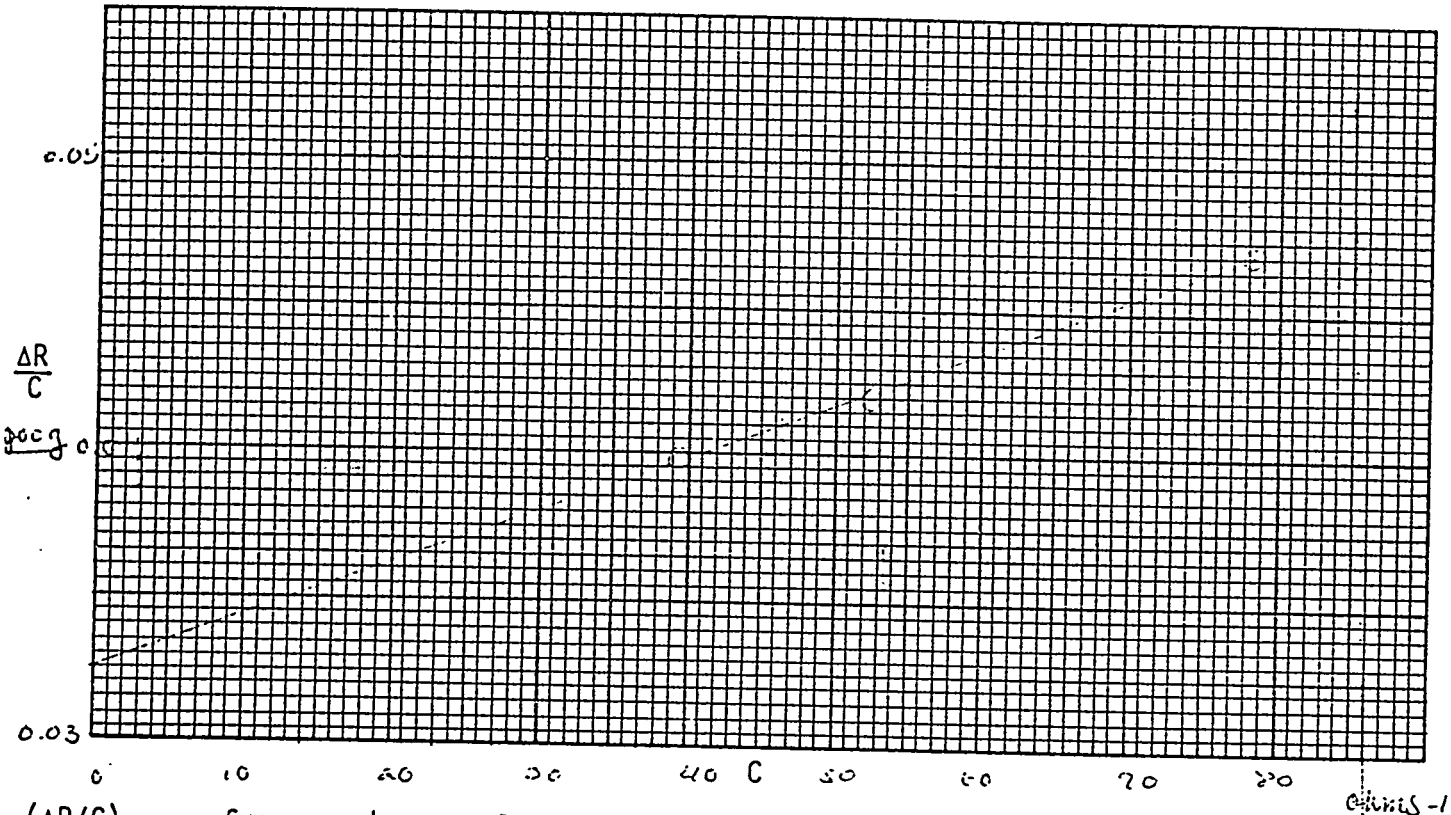
Sample Polypropene Solvent Toluene M_n =

Temperature 37°C. Probe No. _____ Instrument VP

Calibration Standard 10 900 ± 5% = M_N Time Interval 2 min

c = g/100cg of solvent

Concentration, C	39.1296	52.6163	78.2593			Remarks
ΔR	1.53	2.18	3.70			
ΔR	1.56	2.23	3.67			
ΔR	1.56	2.20	3.67			
Average ΔR	1.56	2.21	3.68			
ΔR/C $\times c^2$	3.98675	4.20022	4.70232			



$(\Delta R/C)_{c \to 0}$ from graph 0.0325049 Calibration Factor K = 354.30 grams-1000g / 1 mole

Molecular Weight = $\frac{K}{(\Delta R/C)_{c \to 0}}$ = _____ = _____

Analyst: J. Lechay Date 7/12/68 No: _____

VAPOR PRESSURE OSMOMETERS WORK SHEET

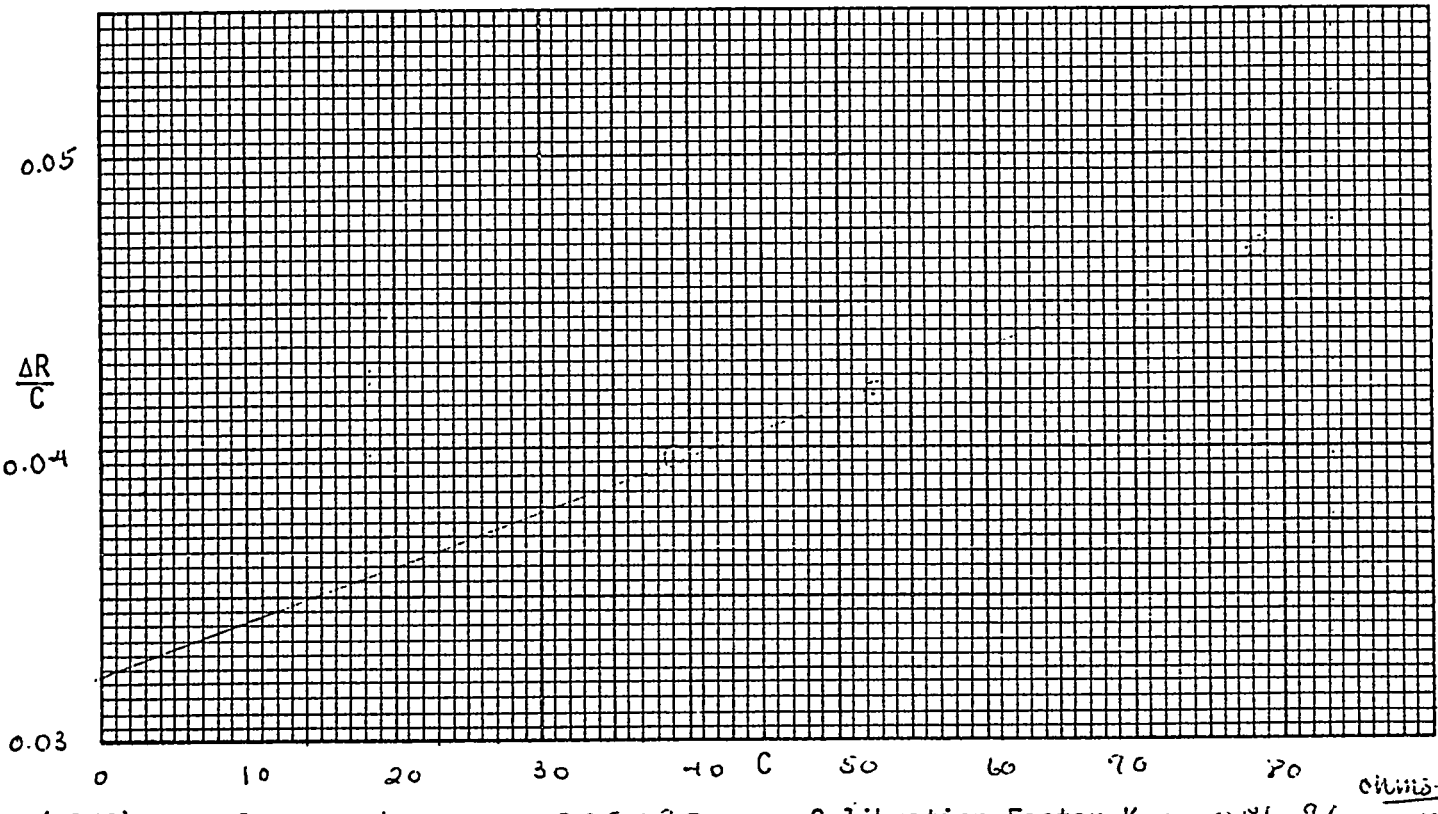
Sample Polystyrene standard Solvent Toluene | M_n =

Temperature 37°C Probe No. _____ Instrument Y P

Calibration Standard 10,900 ± 5% = M_N Time Interval 2 minutes

c = g/1000 g solvent

Concentration, C	39.1296	52.6163	78.2593			Remarks
ΔR	1.53	2.20	3.66			
ΔR	1.55	2.22	3.66			
ΔR	1.57	2.17	3.67			
Average ΔR	1.55	2.20	3.66			
$\Delta R/C \times 10^2$	3.96120	4.18121	4.67676			



$(\Delta R/C)_{c \to 0}$ from graph 0.03229033 Calibration Factor K = 351.96 ohms-1000 g/mole

Molecular Weight = $\frac{K}{(\Delta R/C)_{c \to 0}}$ = _____ = _____

Analyst: J. Lukey Date 7/12/68 No: _____

VAPOR PRESSURE OSMOMETERS WORK SHEET

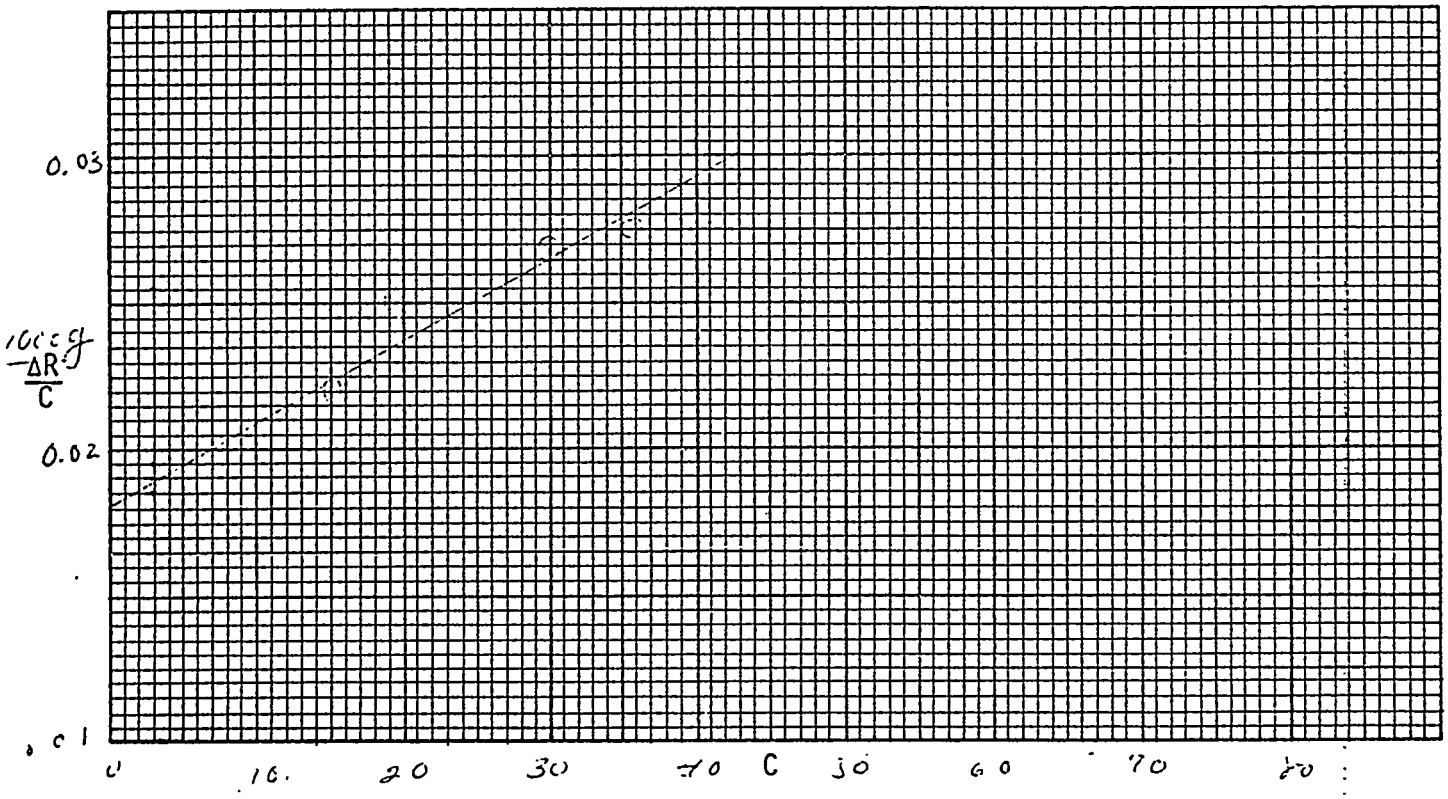
Sample Polyethylene Solvent Toluene M_n = 19,622

Temperature 37°C Probe No. _____ Instrument V.P

Calibration Standard Polystyrene Standard M_n = 10900 Time Interval 2 hrs

± 5%

Concentration, C	14.9805	29.9609	35.7523			Remarks
ΔR	0.33	0.77	1.00			
ΔR	0.34	0.80	0.99			
ΔR	0.33	0.80	0.97			
Average ΔR	0.33	0.80	0.98			
ΔR/C $\times 10^2$	2.20226	2.67014	2.74106			



$(\Delta R/C)_{C \to 0}$ from graph 0.018127 Calibration Factor K = 355.69

Molecular Weight = $\frac{K}{(\Delta R/C)_{C \to 0}}$ = 19,622 = _____

Analyst: J. L. Date 7/16/68 No: _____

VAPOR PRESSURE OSMOMETERS WORK SHEET

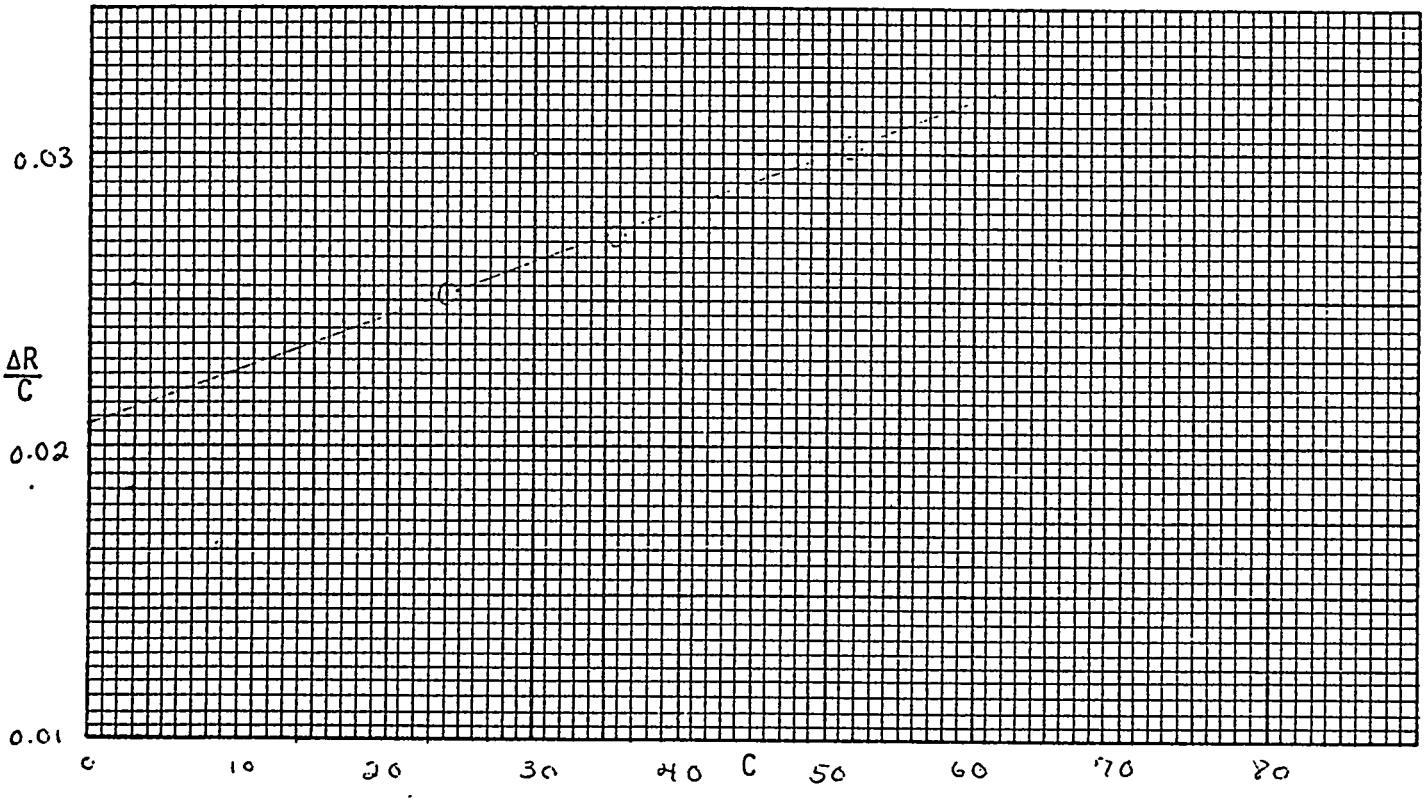
Sample 2300 Polybutylene Solvent Toluene | M_n = 17,115

Temperature 37 °C Probe No. _____ Instrument V.P.

Calibration Standard Polystyrene (M_N = 10,900 ± 5% Time Interval 2 min.

c = g/100cc solvent

Concentration, C	24.1154	35.7523	51.7757			Remarks
ΔR	0.60	0.95	1.55			
ΔR	0.61	0.99	1.58			
ΔR	0.61	0.99	1.59			
Average ΔR	0.61	0.97	1.57			
ΔR/C ×10²	2.52950	2.71311	3.03231			



$(\Delta R/C)_{c \to 0}$ from graph 0.0207788 Calibration Factor K = 355.69

Molecular Weight = $\frac{K}{(\Delta R/C)_{c \to 0}}$ = 17,118 = _____

Analyst: J L Date 7/15/68 No: _____

PROCEDURE FOR MEMBRANE OSMOMETER

I. Preparation of Membrane to Toluene (use either S & S-B-20 or W600). The following procedure was suggested by Arro Laboratories. (It should be noted that the membranes are shipped in an ethanol solution.)

A. Let the membrane soak in the following solutions:

1. 25% ethanol in water solution for 5 hours.
2. 50% ethanol in water solution for 5 hours.
3. 75% ethanol in water solution for 5 hours.
4. 100% ethanol for 6 hours.
5. 25% toluene in ethanol solution for 5 hours.
6. 50% toluene in ethanol solution for 5 hours.
7. 75% toluene in ethanol solution for 5 hours.
8. 100% toluene solution for 6 hours.

Store in 100% toluene.

B. The membrane is 65 mm in diameter, but the cell in the shell model is 51 mm, so it must be cut.

C. Be sure the membrane is never allowed to dry.

II. Installation of a New Membrane:

A. Remove the top and left side cover along with the foam padding.

B. Use a torque wrench to loosen bolts holding the cell (when cell is reassembled, 40 inch pounds should be put on screws).

C. Before placing the membrane on the system of concentric circles, the white O-rings in the center should be replaced. STANDARD TYPE # BY-478.

D. The small black O-rings on each valve must be removed because each solvent requires a special ring. For tolerance use black O-rings #BY-472. If incorrect O-rings are used, the solvent collected in the outlet beaker will be discolored.

E. Rinse the cell off with solvent and replace the block.

F. Remove old solvent in manometer casing through the solvent outlet. Place the new solvent in the funnel, and flush the top of the membrane by injecting 10 cc through the solvent inlet.

III. Preliminary Steps.

Follow the procedure outlined in the manual. Asterisks will indicate the author's additions and emphasis.

A. Open sample inlet valve (1/4 turn counterclockwise).

B. Set servocontrol to manual.

C. Set temperature by adjusting potentiometer to 235 for 36.4°C.

D. Turn on main power switch, set Heat Range to high, and press quick heat. Upon establishing equilibrium the light on Quick Heat goes out.

E. Allow 6 hours for temperature stabilization.

IV. Baseline.

A. Refill the funnel with solvent and again flush the solvent side of cell by injecting 10 cc through the solvent inlet. Remove all air bubbles from solvent syringe prior to injection.

B. Re-adjust solvent to menicus line in manometer.

POLYSTYRENE STANDARD $(\pi/c)^{\frac{1}{2}}$ vs c

Run	c	π/c	$(\pi/c)^{\frac{1}{2}}$	$(\pi/c)^{\frac{1}{2}}_{c\to 0}$	Sxy	$(\pi/c)_{c\to 0}$	M_n
I	0.2157	17.0144	4.1249	4.0702	0.0054	16.5667	18,621
	0.3132	17.1137	4.1369				
	0.3932	17.3703	4.1678				
IV	0.2157	16.5508	4.0683	4.0307	0.0021	16.2461	18,988
	0.3132	16.7305	4.0903				
	0.3932	16.8107	4.1001				
V	0.2157	16.5971	4.0740	4.0024	0.0031	16.0192	19,257
	0.3132	16.9221	4.1136				
	0.3932	17.0905	4.1341				

AVERAGE VALUE OF $\overline{M}_n$ = 18,956 (Based on 3 runs)

$(\pi/c)^{\frac{1}{2}}$ vs c - DIMETHYLPOLYSILOXANE 2300

Run	c	π/c	$(\pi/c)^{\frac{1}{2}}$	$(\pi/c)^{\frac{1}{2}}_{c\to 0}$	Sxy	$(\pi/c)_0$	M_n
I	0.2001	13.9930	3.7407	3.6829	0.002	13.5638	22,743
	0.3872	14.4370	3.7996				
	0.4685	14.5784	3.8182				
II	0.2001	13.9930	3.7407	3.7101	0.00017	13.7648	22,411
III	0.2001	14.4428	3.8004	3.7664	0.002	14.1858	21,746
	0.3872	14.7210	3.8367				
	0.4685	14.7919	3.8460				
IV	0.2001	14.2429	3.7740	3.7682	0.007	14.1993	21,726
	0.3872	14.1529	3.7620				
	0.4685	14.3010	3.7817				
V	0.2001	13.5432	3.6801	3.5525	0.018	12.6203	24,444
	0.3872	14.7469	3.8402				
	0.4685	14.8346	3.8516				
VI	0.2001	14.8426	3.8526	3.8846	0.004	15.0901	20,443
	0.3872	14.6952	3.8334				
	0.4685	14.5144	3.8098				
VII	0.2001	14.7926	3.8461	3.8607	0.002	14.9050	20,697
	0.3872	14.7211	3.8368				
	0.4685	14.6425	3.8266				

AVERAGE VALUE OF $\overline{M}_n$ - 21,628

MEMBRANE OSMOMETRY

DATE 7/5/68

SAMPLE Dimethyl polysiloxane 2300 cstk

SOLVENT Toluene

TEMPERATURE 36.4°C

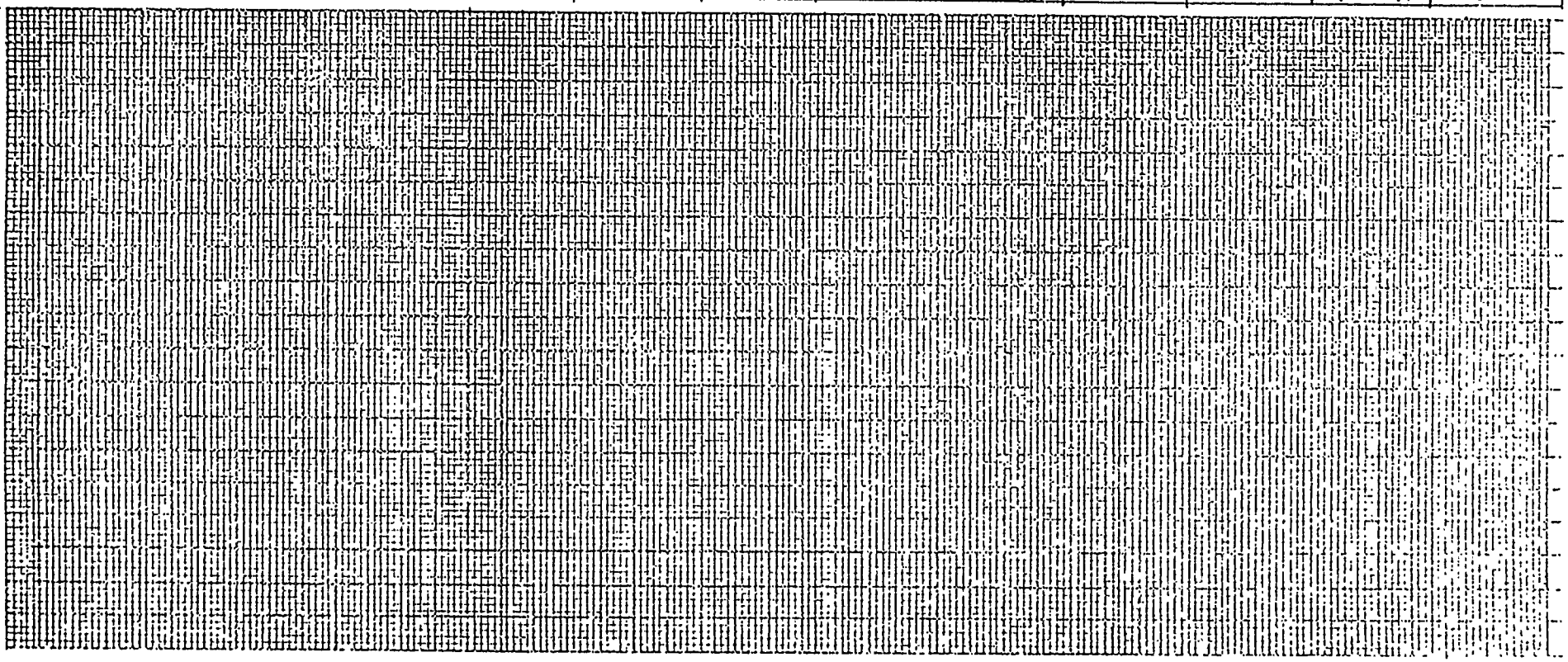
GRAPH NO. P VII

OPERATOR Lutsky

MEMBRANE 600 UL Cellophane

SOLVENT DENSITY 0.8509

	EXTRAPOLATED				AVERAGE of 1ST 5 min			Sxy = 6 067
Concentration @ 100/ML	0.2001	0.3872	0.4685		0.2001	0.3872	0.4685	$\bar{I}_E$ = 15. 6563
P	3.57	6.07	7.29		3.26	6.00	7.16	MW_E = 19,645
Base Line, Po, Cm.	.30	.30	.30		.30	.30	.30	Sxy = 0.015
π = P-Po	3.07	5.77	6.99		2.96	5.70	6.86	$\bar{I}_A^0$ = 14. 90469
π/c	15.3423	14.9019	14.9200		14.7426	14.7211	14.6125	MW_A = 20, 688



MEMBRANE OSMOMETRY

DATE 7/29/68

GRAPH NO. R-I

SAMPLE Dimethylsiloxane 8000 cstk

OPERATOR Luthy

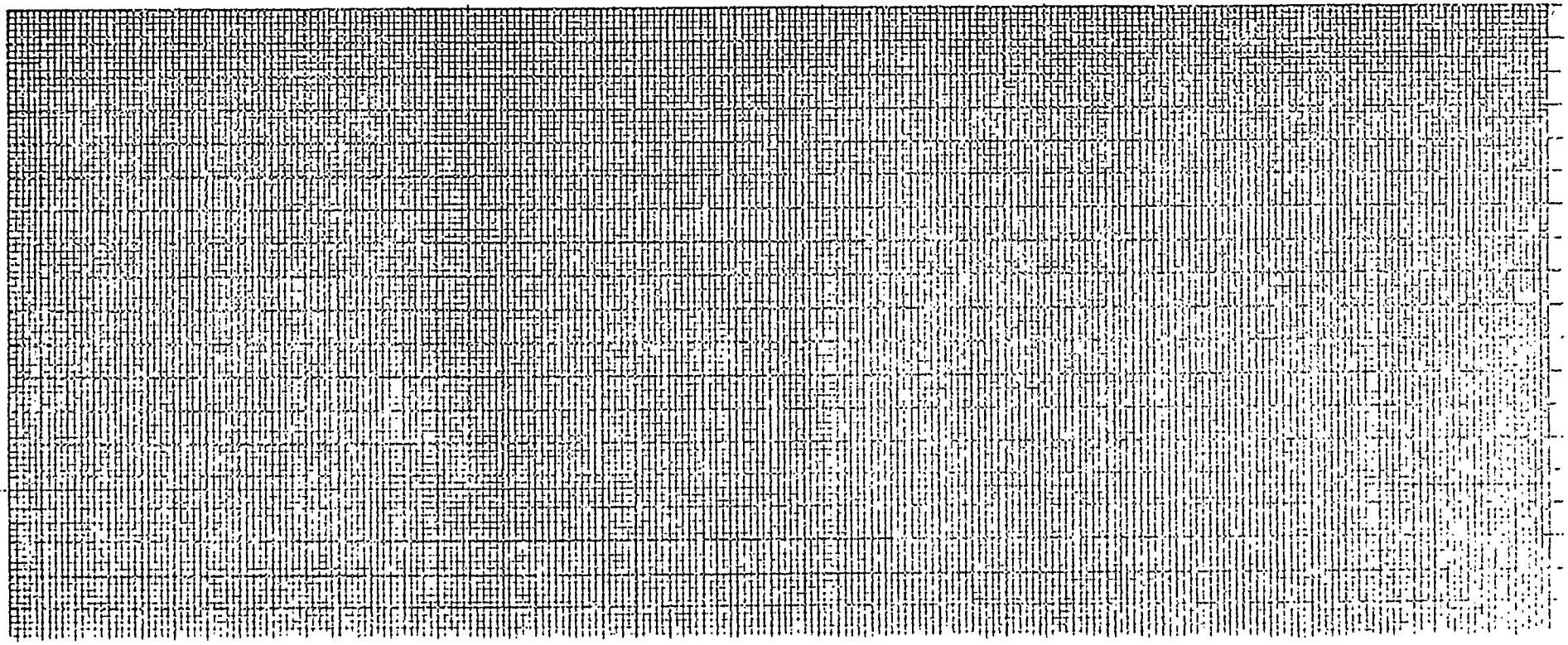
SOLVENT Toluene

MEMBRANE 600 EC Ultrafine

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8509

Concentration @ 100/ML	0.2000	0.3310	0.4113	0.5081			INTERCEPT =	11.7209	
P	2.54	3.96	4.75	5.72			ST. DEVIATION =	0.065	
Base Line, Po, Cm.	0.28	0.28	0.28	0.28			MOL. WEIGHT =	26,307.	
π = P-Po	2.26	3.68	4.47	5.44					
π/c	11.3000	11.1178	10.8680	10.7066					



MEMBRANE OSMOMETRY

DATE 7/30/68

SAMPLE Dimethylpolysiloxane 8000 cstk

SOLVENT Toluene

TEMPERATURE 36.4 °C

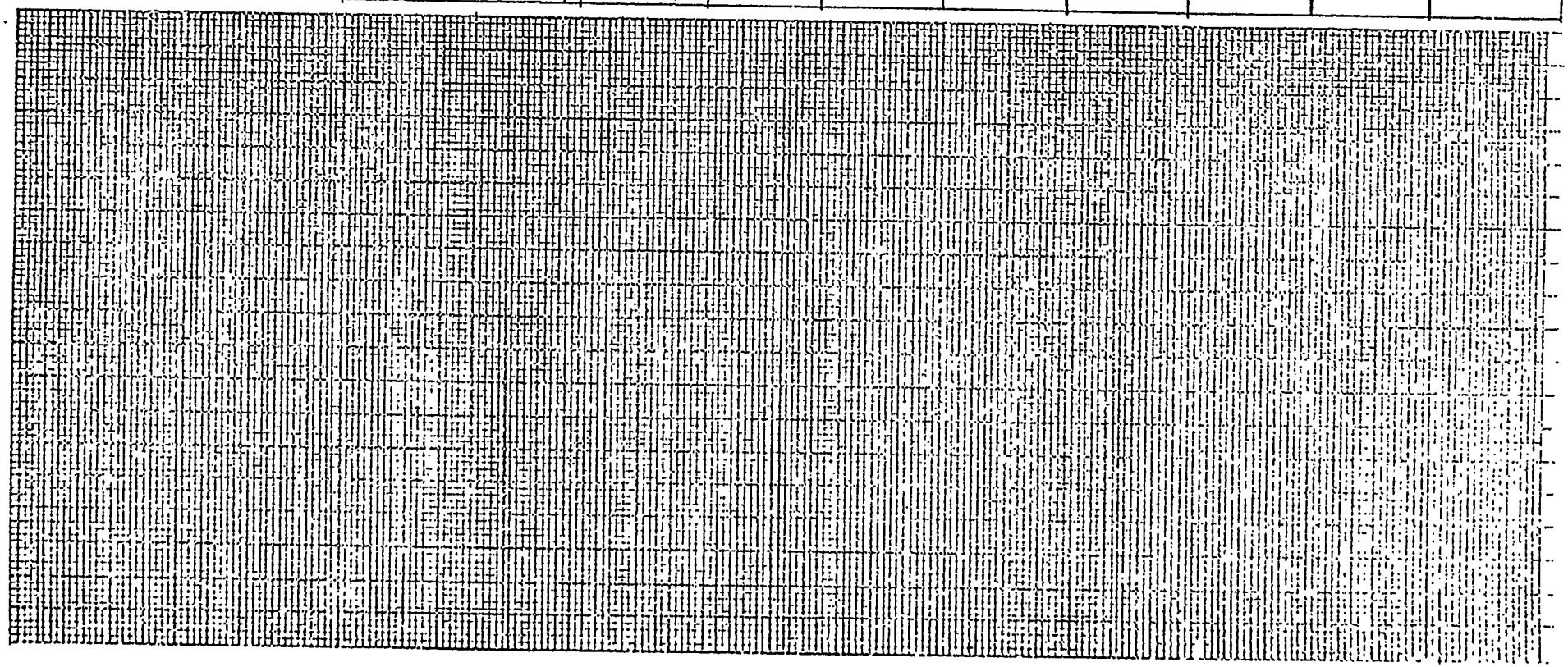
GRAPH NO. PIII

OPERATOR Lusby

MEMBRANE 600 Hc Cellophane

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2000	0.3310	0.4113	0.5081		I = 11.6436				
P	2.51	3.97	4.77	5.77		Sxy = 0.056				
Base Line, Po, Cm.	.25	.25	.25	.25		M_N = 26,494				
π = P-Po	2.26	3.72	4.52	5.52						
π/c	11.300	11.2387	10.9842	10.8640						



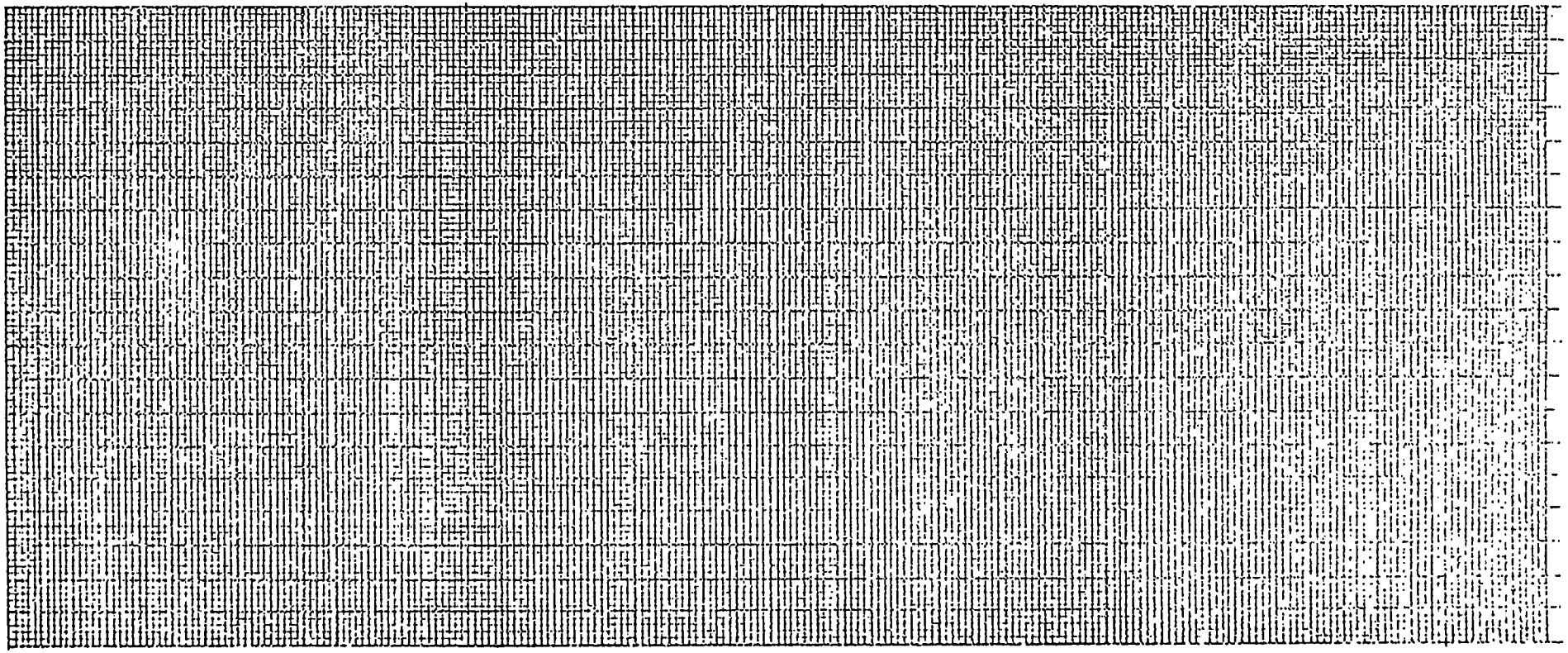
DATE 8/1/68 GRAPH NO. R-IV

SAMPLE Dimethylpolysiloxane 2000 cstk OPERATOR Lusby

SOLVENT Toluene MEMBRANE 600 Mil Cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

Concentration @ 100/ML	.2000	0.3310	0.4113	0.5081						
P.	2.58	4.00	4.75	5.78						
Base Line, Po, Cm.	.27	.27	.27	.27				I = 12.0338		
π = P-Po	2.31	3.73	4.48	5.51				M.W = 25,635.		
π/c	11.5560	11.2689	10.8923	10.8443						



MEMBRANE OSMOMETRY

DATE 8/1/68 GRAPH NO. RV

SAMPLE Dimethyl polysiloxane 8000 cstk OPERATOR [illegible]

SOLVENT Toluene MEMBRANE 600 Regenerated Cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2000	0.3310	0.4113	0.5081						
P	2.67	4.06	4.93	5.97		$\bar{Y}$ =	11.6146			
Base Line, Po, Cm.	.39	.39	.39	.39		M_N =	26,561			
π = P-Po	2.28	3.67	4.54	5.58		S_{xy^2}	0.057			
π/c	11.400	11.0896	11.0382	10.9829						

MEMBRANE OSMOMETRY

DATE 8/ /16

GRAPH NO. RVI

SAMPLE Dimethylpolysiloxane 8000 cstk

OPERATOR Luthey

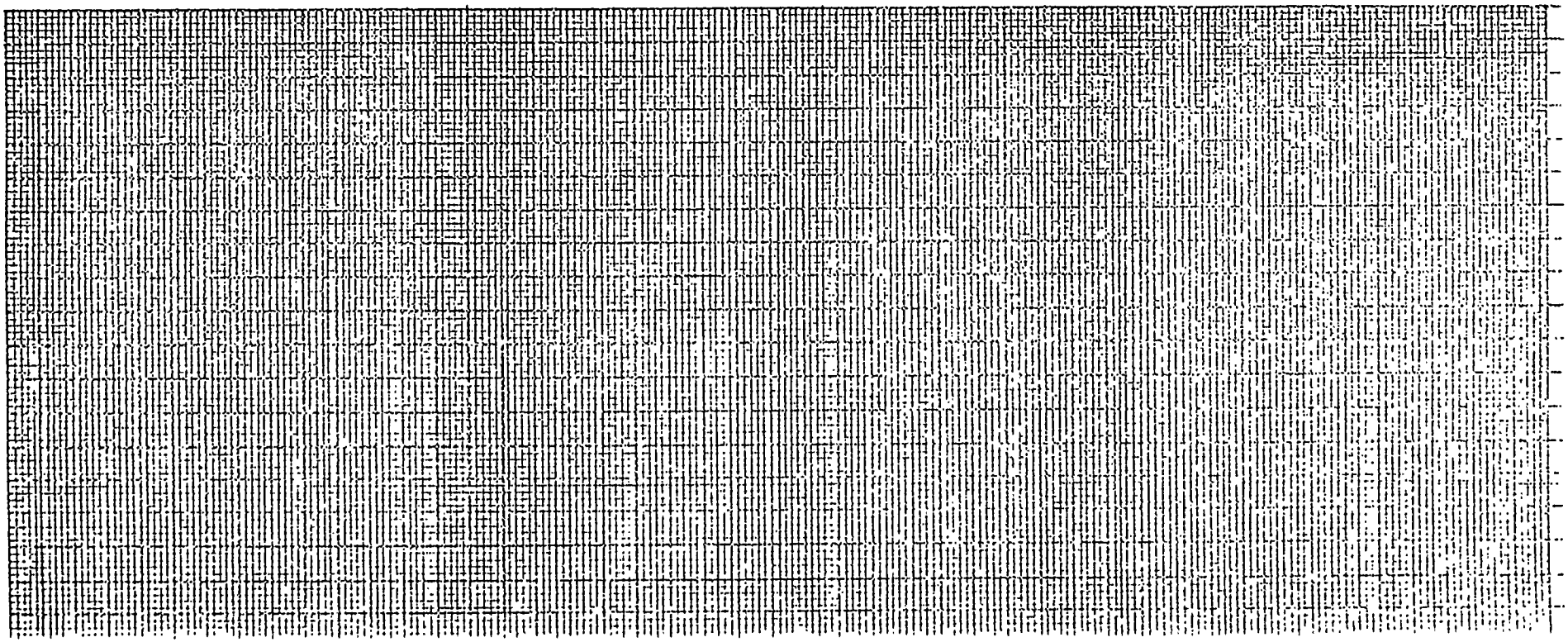
SOLVENT Toluene

MEMBRANE 600 Å Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2600	0.3310	0.4113	0.5081						
P	2.67	4.09	4.90	5.93						
Base Line, Po, Cm.	.83	.83	.83	.83			Γ =	11.7058		
π = P-Po	2.28	3.76	4.57	5.60			M_N =	26,354.		
π/c	11.4000	11.3595	11.1111	11.0215						



MEMBRANE OSMOMETRY

DATE 7/8/68

GRAPH NO. I

SAMPLE M#1 - DMPS 2300/8200

OPERATOR Leahey

SOLVENT Toluene

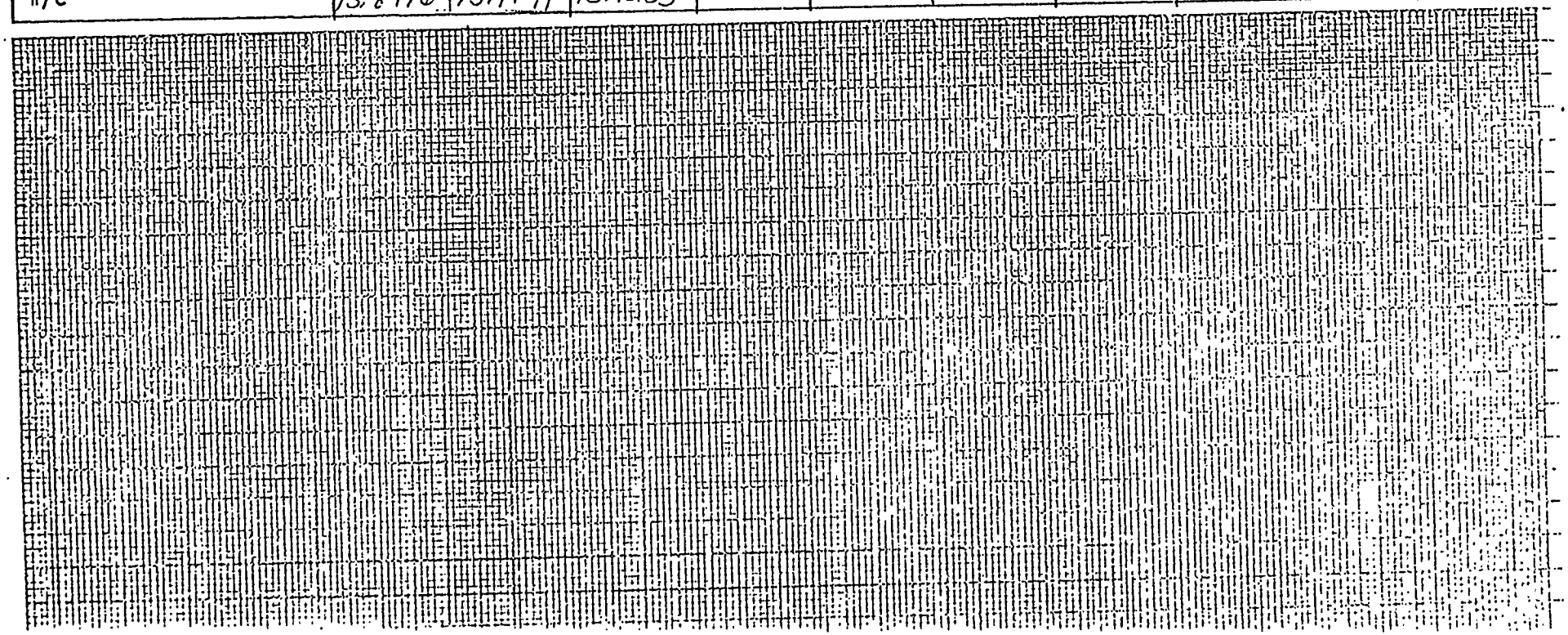
MEMBRANE 600 Nel Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8509

No extrapolation

Concentration @ 100/ML	0.2030	0.3099	0.4015					$\bar{I}$ = 14.041369	
P	3.07	4.50	5.76					$\bar{M}\bar{W}$ = 21,960	
Base Line, Po, Cm.	.25	.25	.25					δ_{xy} = 0.041	
π = P-Po	2.82	4.25	5.51						
π/c	13.8916	13.7141	13.7235						



MEMBRANE OSMOMETRY

DATE 8/16/67

SAMPLE Mix #1 - DMPS

SOLVENT Toluene

TEMPERATURE 36.4°C

GRAPH NO. π

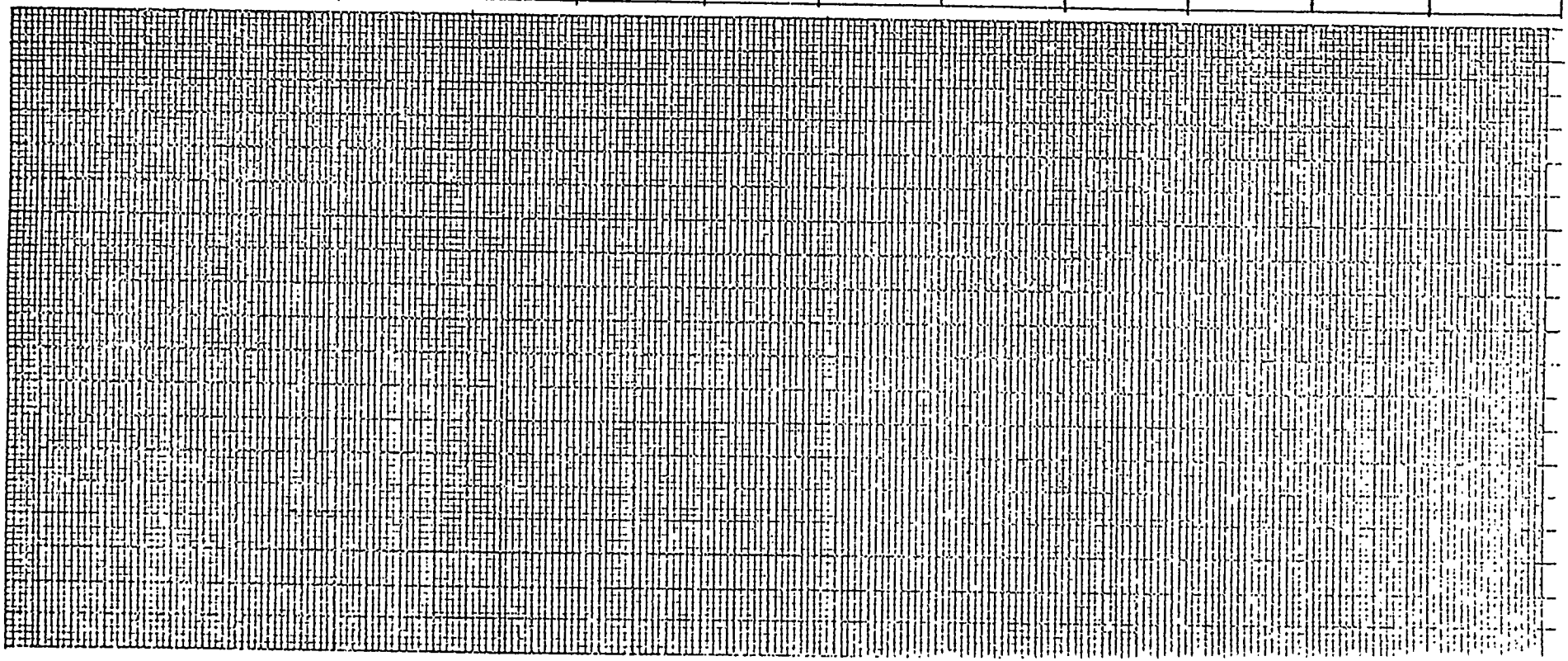
OPERATOR Leahy

MEMBRANE 600 Cellophane

SOLVENT DENSITY 0.8505

Extrapolation

Concentration @ 100/ML	0.2030	0.3099	0.4015				I =	13 63 728		
P	3.15	4.72	6.07				S_{xy} =	0.025		
Base Line, Po, Cm.	.31	.31	.31				M_N =	22,619		
π = P-Po	2.84	4.41	5.76							
π/c	13.4901	14.2304	14.3462							



MEMBRANE OSMOMETRY

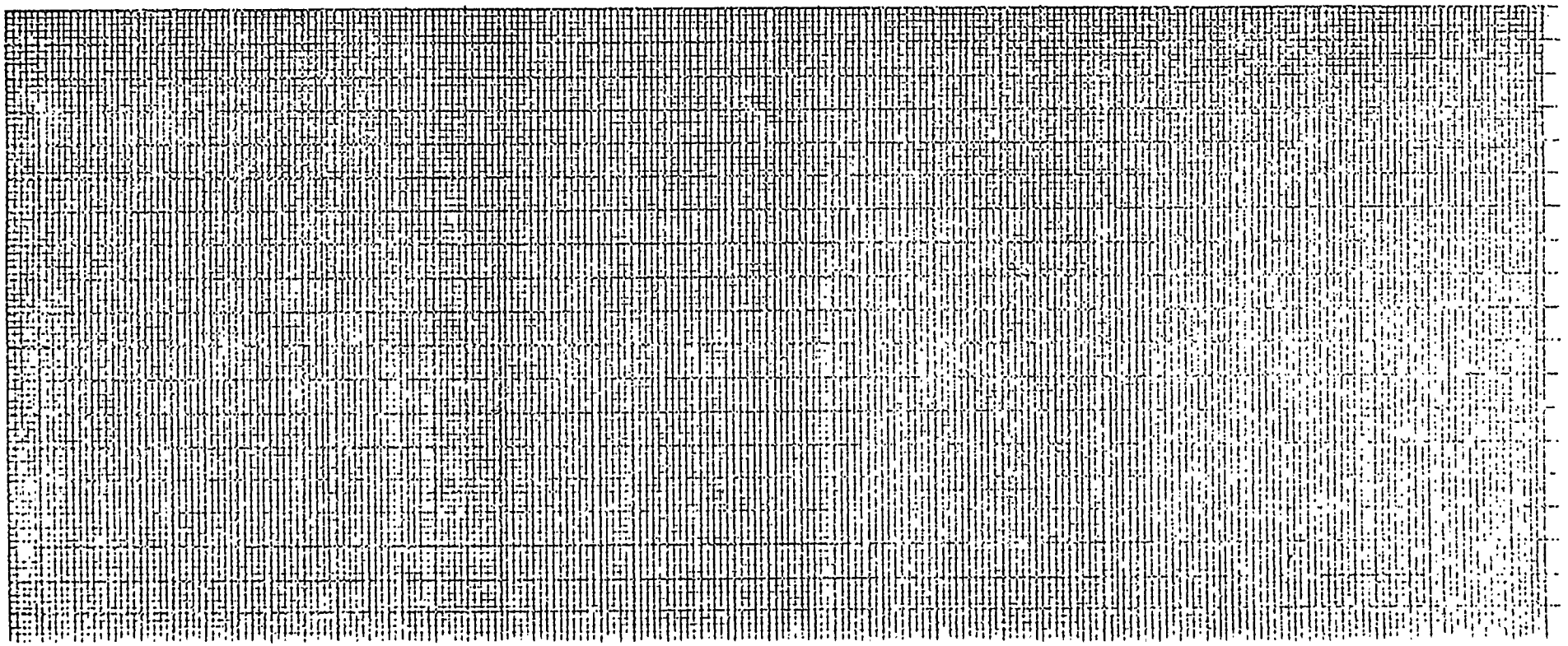
DATE 7/23/68 GRAPH NO. IV

SAMPLE Polystyrene (M.W-19,800) OPERATOR Lutley

SOLVENT Toluene MEMBRANE 600 Å Collodion

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8669

Concentration @ 100/ML	0.1866	0.2157	0.3132	0.3932			INTERCEPT =	16.242	82
P	3.60	4.57	6.29	7.61			MOL. WEIGHT =	19,994	
Base Line, Po, Cm.	1.0	1.0	1.0	1.0					
π = P-Po	2.6	3.57	5.24	6.61					
π/c	16.6028	16.5508	16.7305	16.8107					



MEMBRANE OSMOMETRY

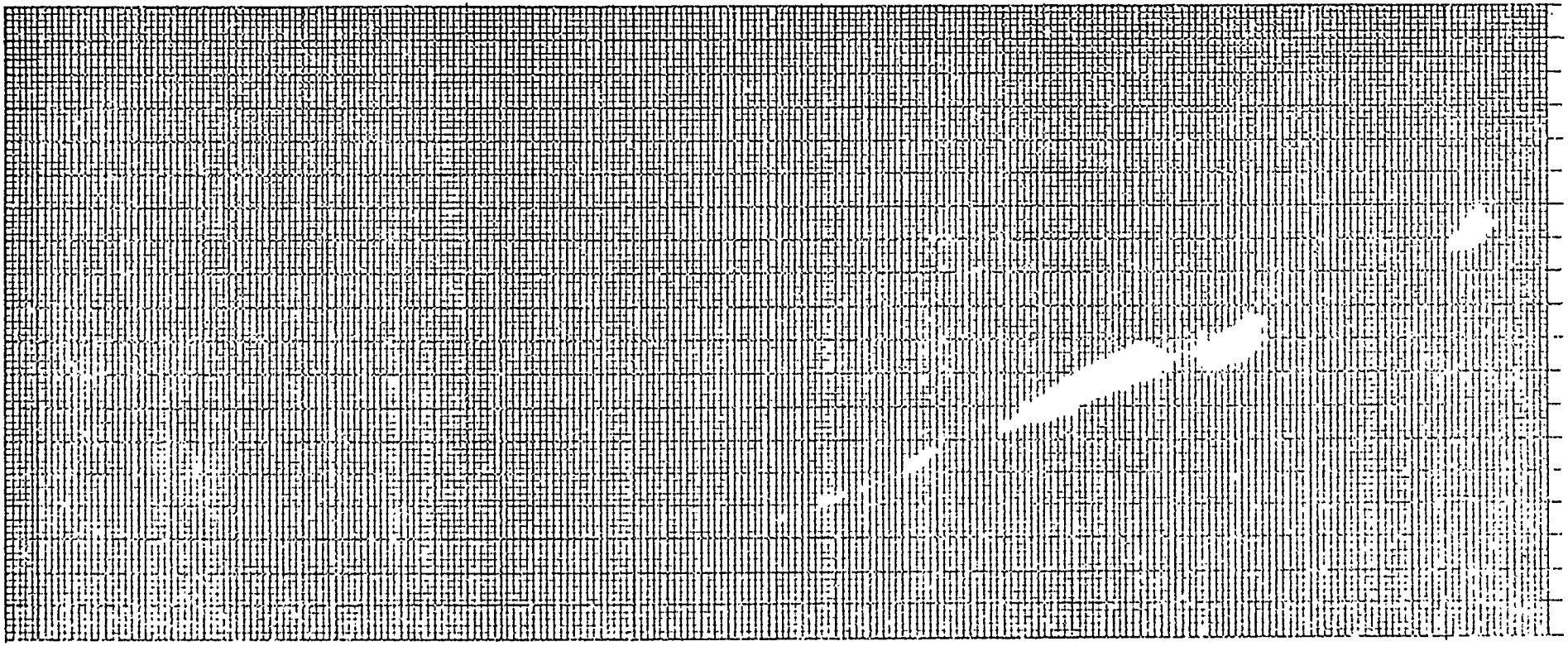
DATE 7/23/68 GRAPH NO. V

SAMPLE Polystyrene Standard M.W. = 19,800 OPERATOR Linley

SOLVENT Toluene MEMBRANE 600 Sel Cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

Concentration @ 100/ML	~~0.1566~~	0.2157	0.3132	0.3932				I =	16.0094	
P	~~2.87~~	3.80	5.52	6.94				M_W =	19,272	
Base Line, Po, Cm.	~~.22~~	.22	.22	.22						
π = P-Po	~~2.65~~	3.58	5.30	6.72						
π/c	~~16.9221~~	16.59712	16.9221	17.0905						



MEMBRANE OSMOMETRY

DATE 7/24/68

GRAPH NO. I

SAMPLE DMPS-2300

OPERATOR Lusby

SOLVENT Isomin

MEMBRANE 600 Sel cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2001	0.3872	0.4685				I= 13.55 68	
P	3.23	6.02	7.26				S_{xy} = 0.016	
Base Line, Po, Cm.	.43	.43	.43				M= 22.755	
π = P-Po	2.80	5.59	6.83					
π/c	13.9930	14.4370	14.5784					

MEMBRANE OSMOMETRY

DATE 7/24/68

SAMPLE DMPS -2300

SOLVENT Toluene

TEMPERATURE 36.4°C

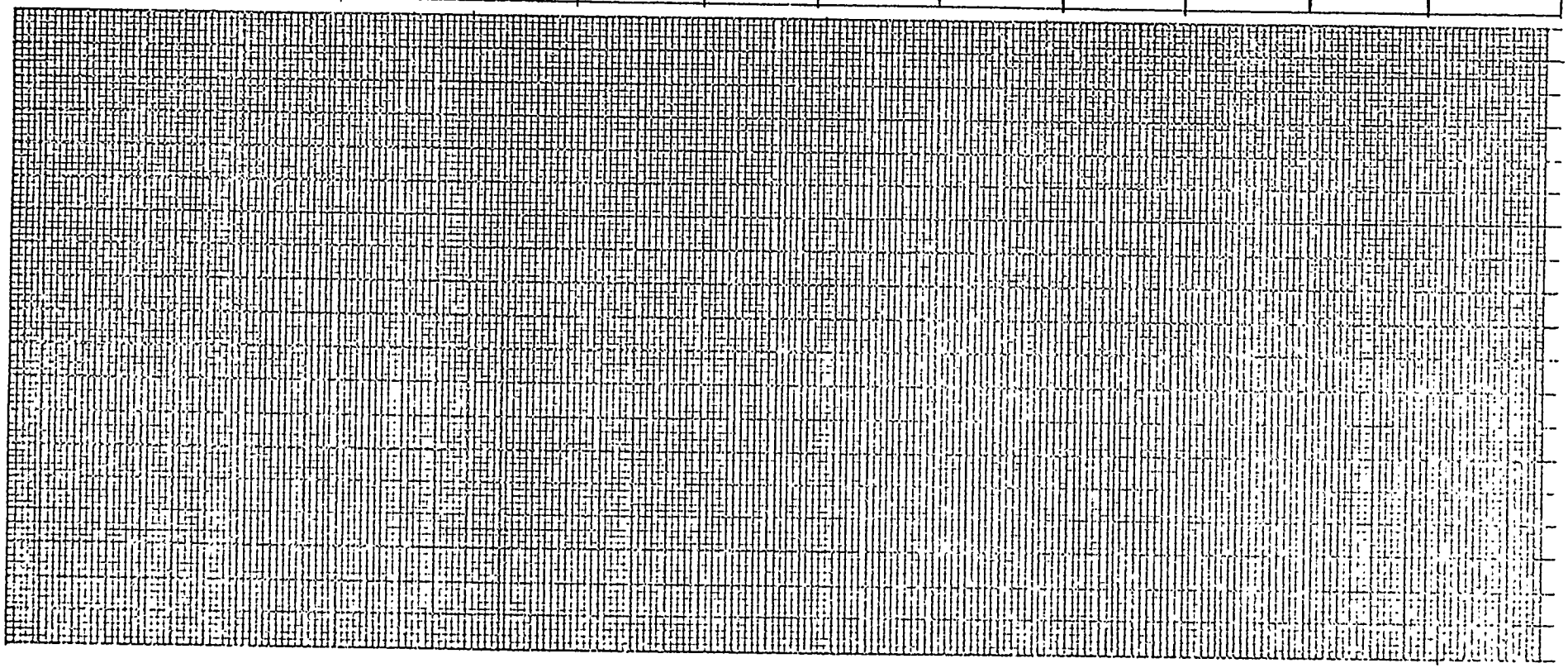
GRAPH NO. π

OPERATOR Purdy

MEMBRANE 600 Del Cellophane

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2001	0.3872	0.4685				I =	13.7634		
P	3.15	5.85	7.05				Σxy =	0.0015		
Base Line, Po, Cm.	.35	.35	.35				M =	22.414		
π = P-Po	2.80	5.50	6.80							
π/c	13.9930	14.2045	14.3010							



MEMBRANE OSMOMETRY

DATE 7/24/68

GRAPH NO. III

SAMPLE DMPS 2300

OPERATOR Lucky

SOLVENT Toluene

MEMBRANE 600 Gel Cellophane

TEMPERATURE 36.4 °C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	c. 2001	o 3872	0.4685				I =	14.182	7	
P	3.24	6.05	7.28				δx_y = 0.016			
Base Line, Po, Cm.	.35	.35	.35				M = 21.7	51		
π = P-Po	2.89	5.70	693							
π/c	14.4428	14.7210	14.7919							

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MEMBRANE OSMOMETRY

DATE 7/25/68

GRAPH NO. Run IV

SAMPLE DMPS -2300

OPERATOR Lusby

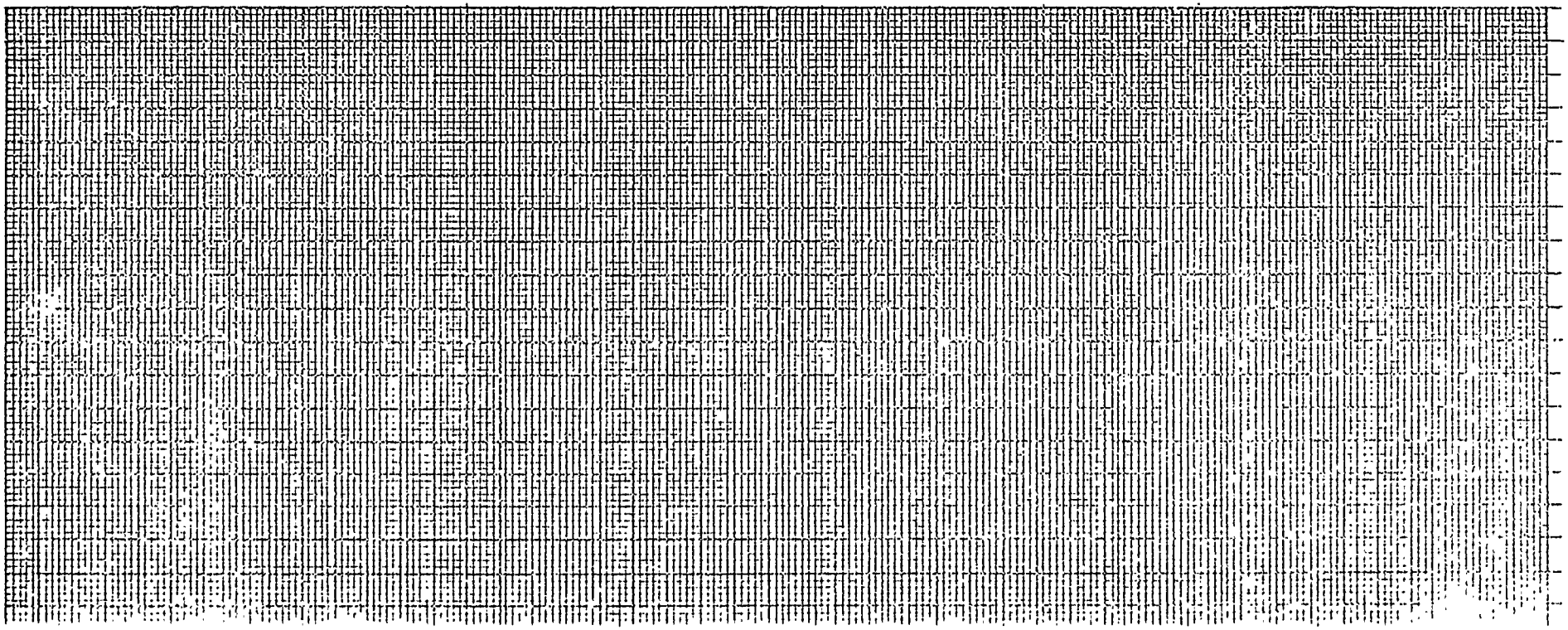
SOLVENT Toluene

MEMBRANE 600 Sil Microfilm

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2001	0.3872	0.4685				I =	14.19	88	
P	3.08	5.71	6.93				δx_c = 0.060			
Base Line, Po, Cm.	.23	.23	.23				M_v^0 = 21,727			
π = P-Po	2.85	5.48	6.70							
π/c	14.2429	14.1529	14.3010							



MEMBRANE OSMOMETRY

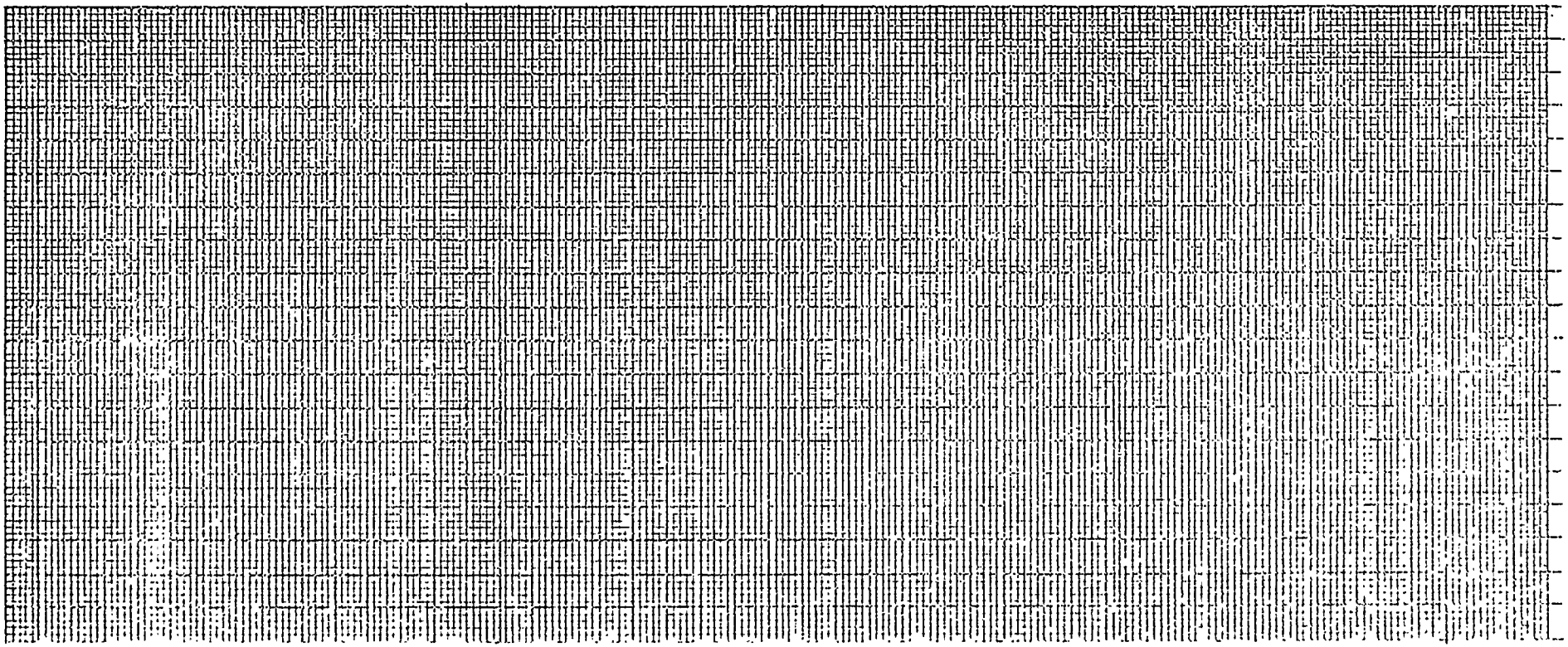
DATE 7/25/68 GRAPH NO. RV

SAMPLE DMPS -2300 OPERATOR Lusby

SOLVENT Toluene MEMBRANE 600 Sel Cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2001	0.3872	0.4685				I=	12.5822		
P	3.73	6.73	7.97				S_{xy}=	0.14		
Base Line, Po, Cm.	1.02	1.02	1.02				M=	24,518		
π = P-Po	2.71	5.71	6.95							
π/c	13.5432	14.7469	14.8346							



MEMBRANE OSMOMETRY

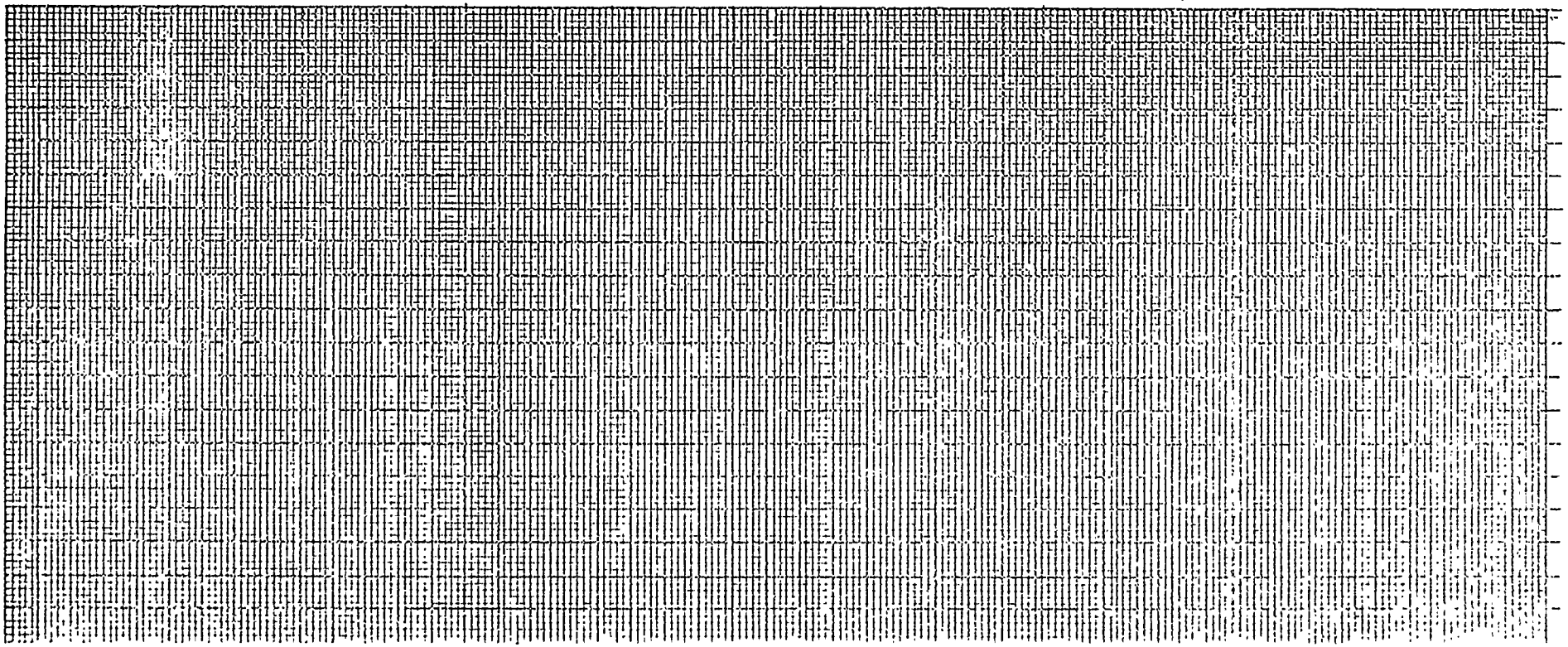
DATE 2/5/68 GRAPH NO. R VI

SAMPLE DMPS - 2300 calc OPERATOR [illegible]

SOLVENT toluene MEMBRANE 600 Pat cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

	Extrapolated				average of 1st 5 min.				I_E = 16.2365	
Concentration @ 100/ML	0.2001	0.3872	0.4685		0.2001	0.3872	0.4685		S_{xy} = 0.	0048
P	3.45	6.13	7.23		3.30	6.02	7.13		M_N = 19	,000
Base Line, Po, Cm.	.33	.33	.33		.33	.33	.33		I_A = 15	.8774
π = P-Po	3.12	5.80	6.90		2.97	5.69	6.80		S_{xy} = 0.	037
π/c	15.5922	14.9793	14.7279		14.8426	14.6952	14.5144		M_N = 2	0,446



MEMBRANE OSMOMETRY

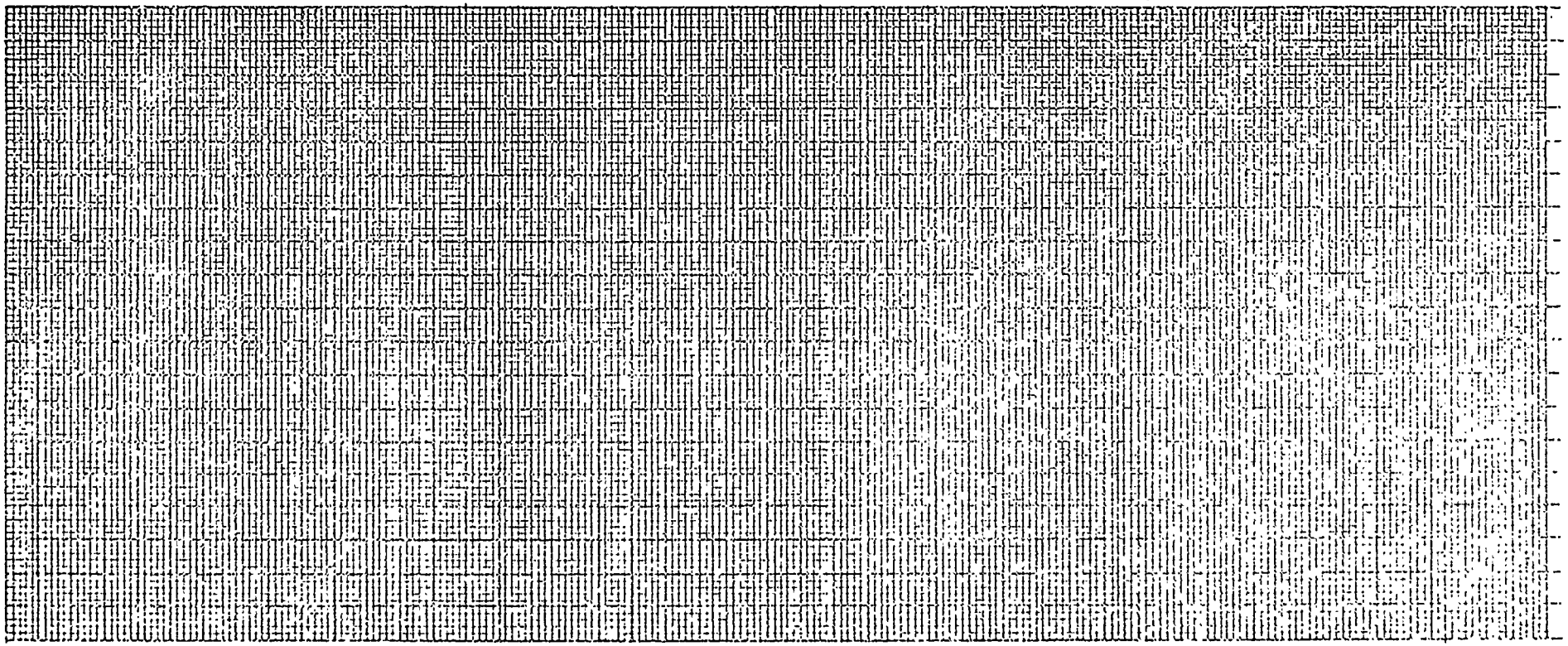
DATE 8/6/68 GRAPH NO. II

SAMPLE MF#1-DMPS 2300/8000 OPERATOR Lurkey

SOLVENT Toluene MEMBRANE 600 Sel Cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2030	0.3099	0.4015					I = 13.6378		
P	3.12	4.64	5.95					M.W =	22,620	
Base Line, Po, Cm.	.31	.31	.31					S_{xy} =	0.009	2
π = P-Po	2.81	4.33	5.64							
π/c	13.8424	13.9722	14.0473							



MEMBRANE OSMOMETRY

DATE 2/7/68

GRAPH NO. III

SAMPLE Mixture #1 DMPS 2300/8000

OPERATOR Lemley

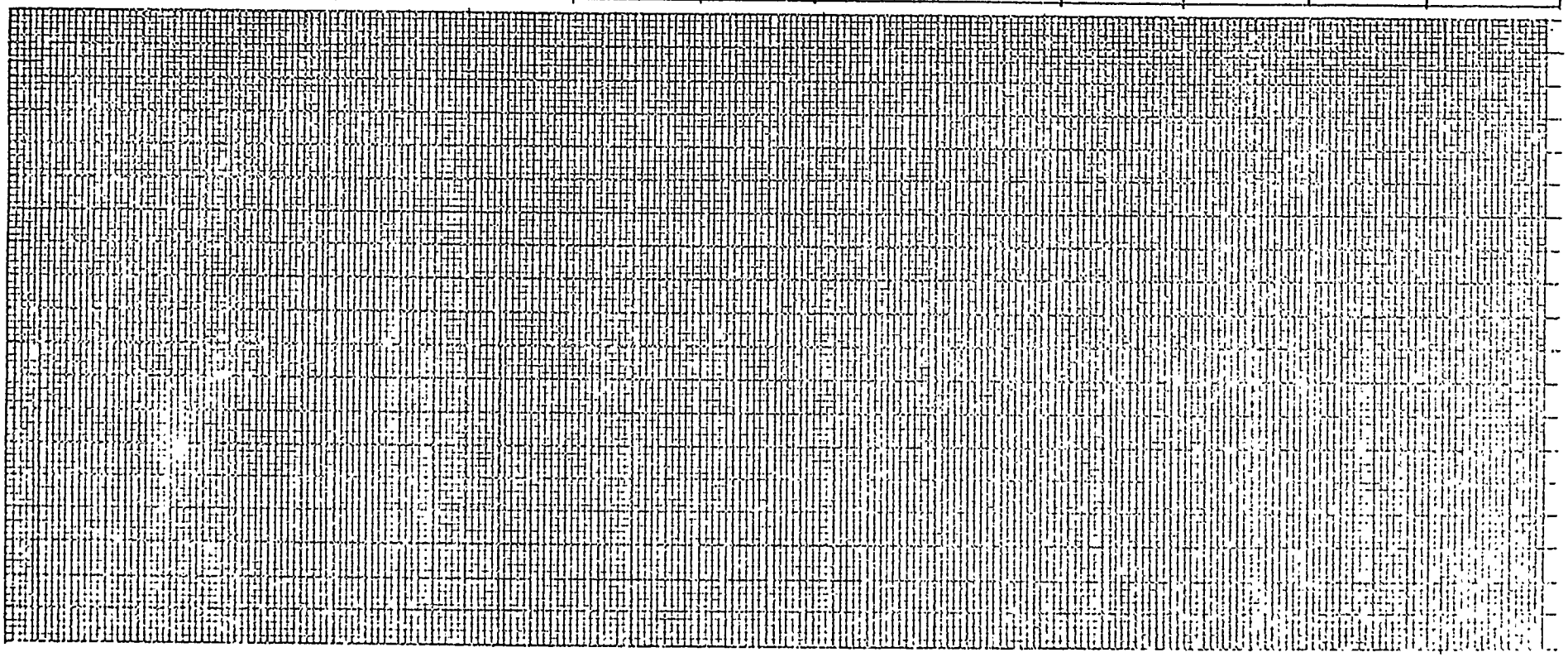
SOLVENT Toluene

MEMBRANE 600 Hot

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2030	0.3099	0.4015				I =	13.86	65.6	
P	3.09	4.64	5.90				δ_{xy} =	0.064		
Base Line, Po, Cm.	.26	.26	.26				M_N =	22,247		
π = P-Po	2.83	4.38	5.64							
π/c	13.9409	14.1336	14.0473							



DG-120

MEMBRANE OSMOMETRY

DATE 8/17/68

GRAPH NO. III

SAMPLE Dimethylpolysiloxane Mix #1

OPERATOR Lurkey

SOLVENT Toluene

MEMBRANE 600 Lot Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY C.8505

Extrapolated

Concentration @ 100/ML	0.2030	0.3099	0.4015				I =	14.34467		
P	3.17	4.73	6.02				δxy =	0.038		
Base Line, Po, Cm.	.26	.26	.26				M_N =	21,506		
π = P-Po	2.91	4.47	5.76							
π/c	14.3350	14.4240	14.3762							

MEMBRANE OSMOMETRY

DATE 2/8/68

GRAPH NO. I

SAMPLE Harvard # 2 DMPS

OPERATOR Lusby

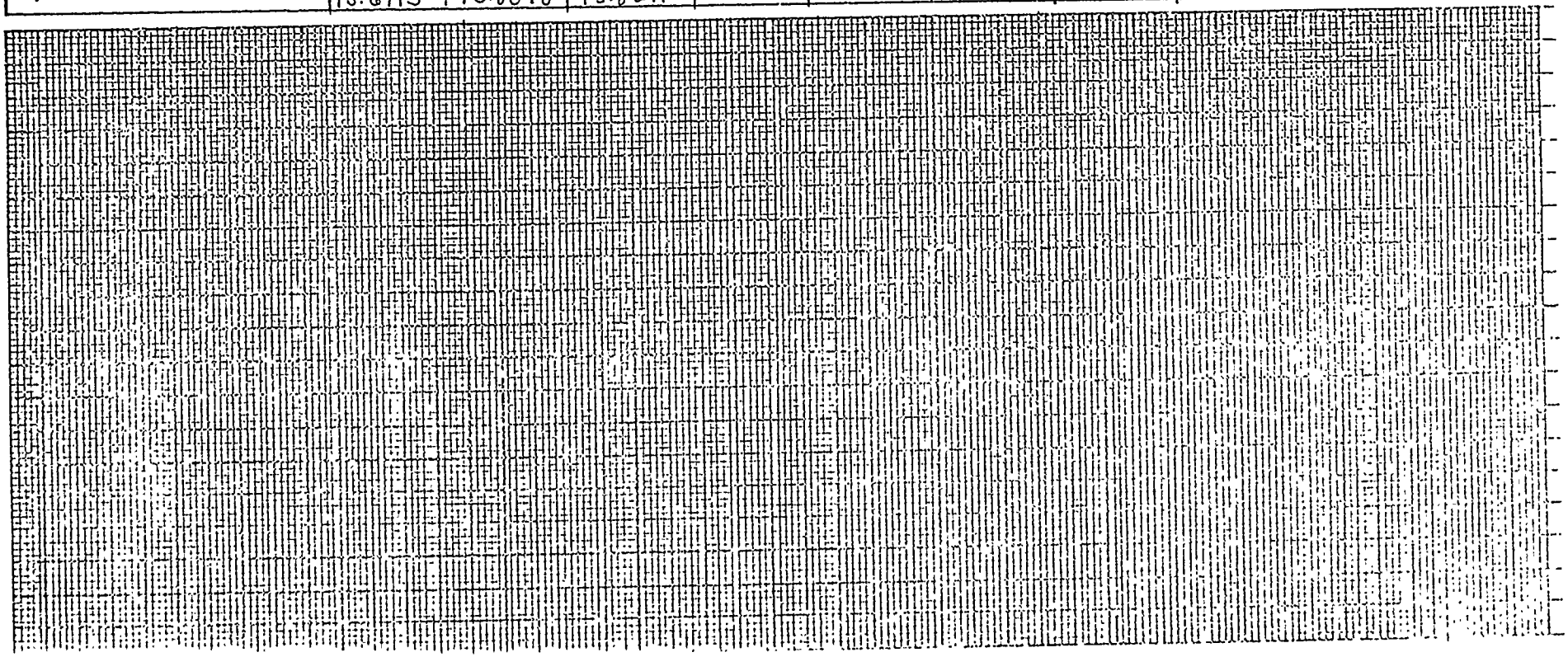
SOLVENT Toluene

MEMBRANE 600 Gel Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2013	0.3288	0.4305				I = 1	3.44566		
P	3.01	4.81	6.22				M_N =	22,941		
Base Line, Po, Cm.	.27	.27	.27				δ_{xy} =	0.037		
π = P-Po	2.74	4.54	5.95							
π/c	13.6115	13.8078	13.8211							



DG-120

MEMBRANE OSMOMETRY

DATE 8/18/68

GRAPH NO. II

SAMPLE Nitride #2 DMPS

OPERATOR Lutby

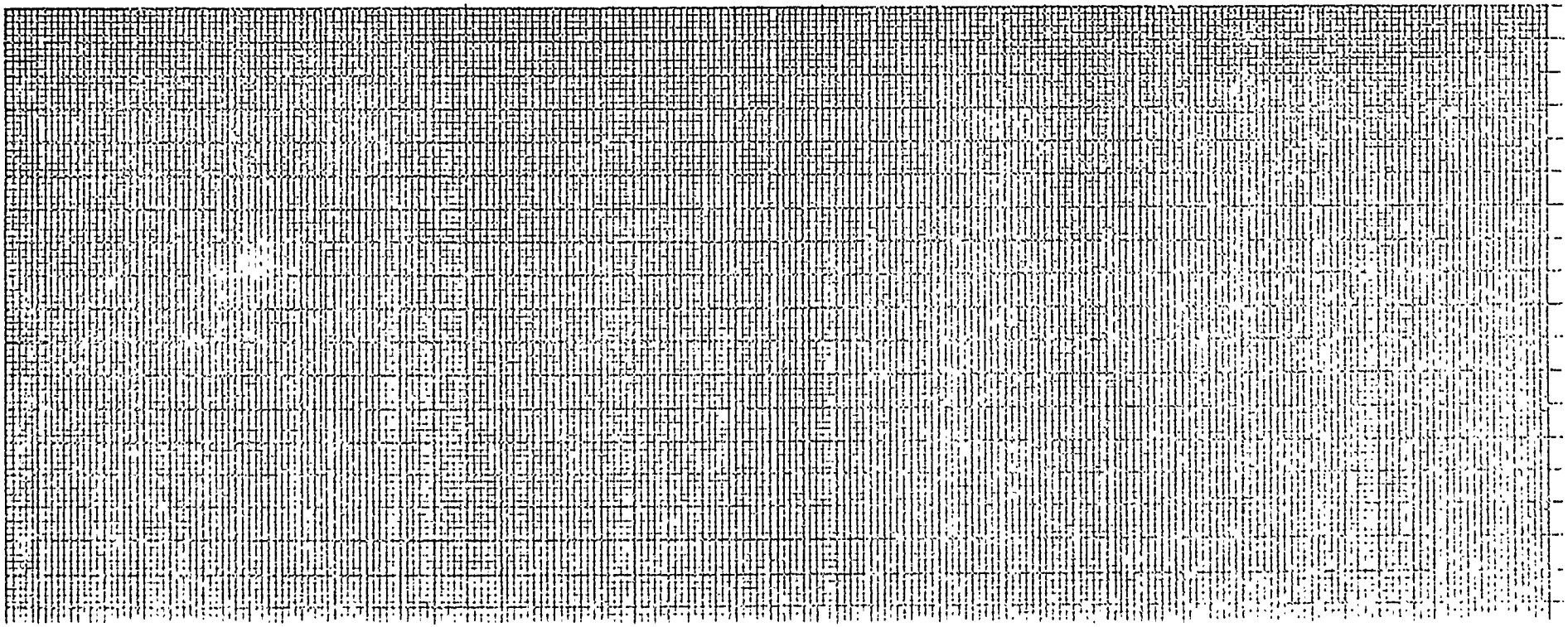
SOLVENT Toluene

MEMBRANE 600 Sel Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2013	0.3288	0.4305	0.5168			I =	13,47	468987	
P	3.01	4.83	6.24	7.42			MW=	22,894		
Base Line, Po, Cm.	.28	.28	.28	.28			S_{xy}=	0.0728		
π = P-Po	2.73	4.55	5.96	7.14						
π/c	13.5618	13.8382	13.8444	13.8158						



DG-120

MEMBRANE OSMOMETRY

DATE 8/8/68

GRAPH NO. III

SAMPLE MW#2 OMPS

OPERATOR Luckey

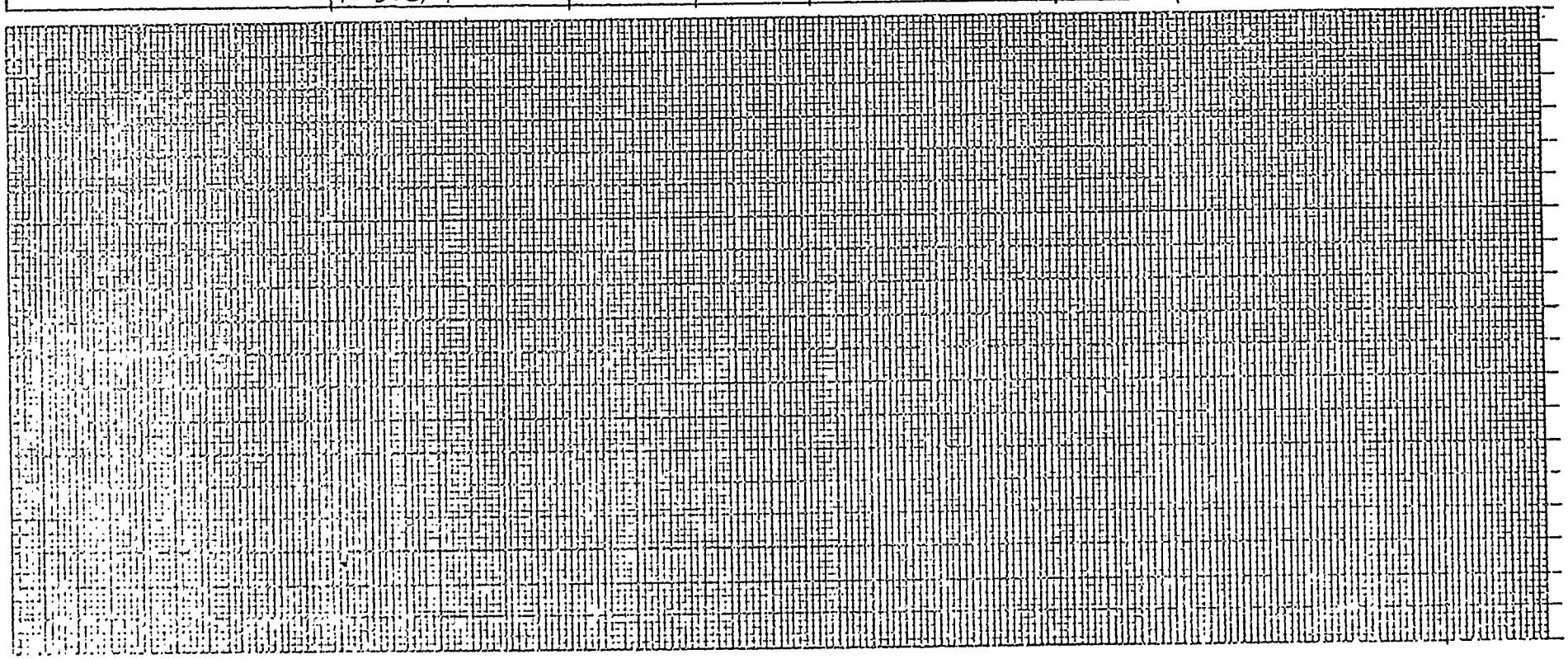
SOLVENT Toluene

MEMBRANE 600 Nel Cellophane

TEMPERATURE 36.4 °C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2013	0.3288	0.4305	0.5168			$\bar{I}$ =	12.96344	
P	3.09	5.01	6.38	7.77			S_{xy} =	0.1485	
Base Line, Po, Cm.	.40	.40	.40	.40			M_N =	23,796	
π = P-Po	2.69	4.61	5.98	7.37					
π/c	13.3631	14.0207	13.8908	14.2608					



MEMBRANE OSMOMETRY

DATE 8/12/68

GRAPH NO. I

SAMPLE Dimethylpolysiloxane Mix #3

OPERATOR Lustley

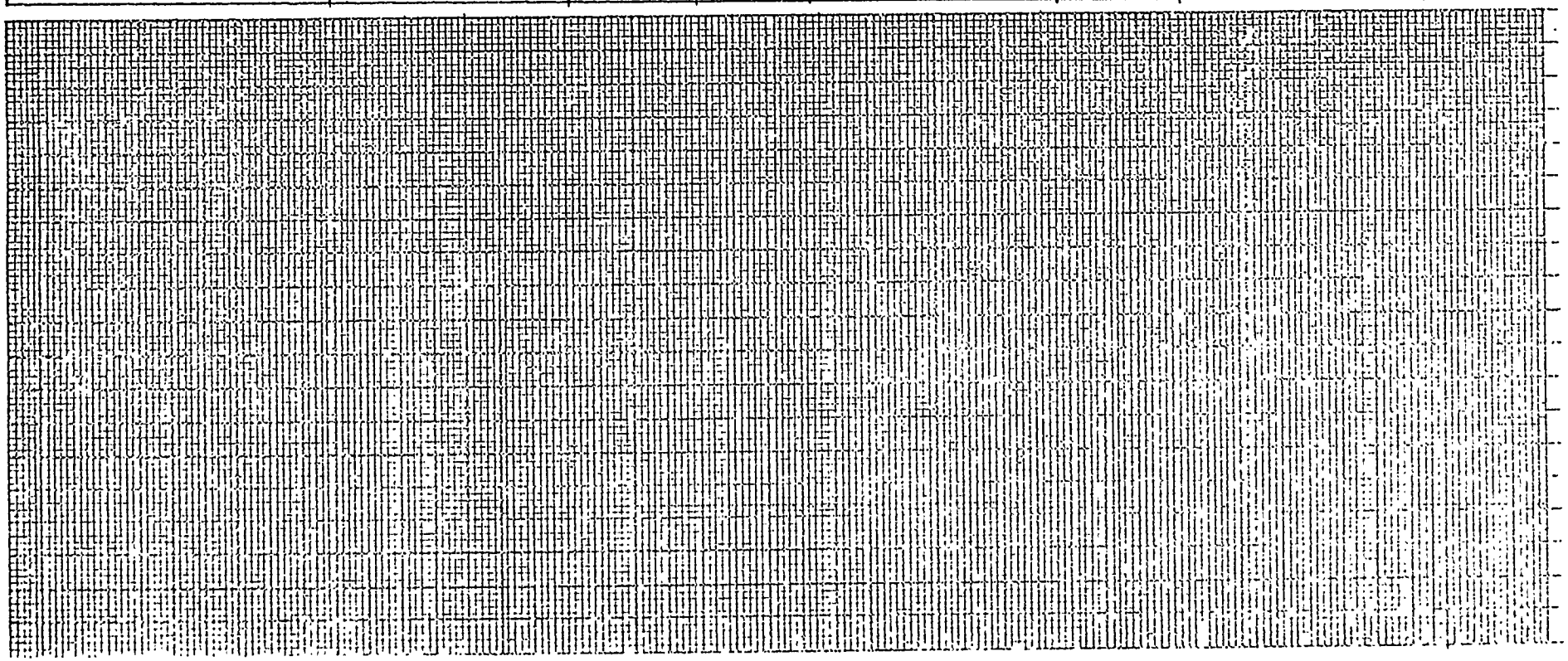
SOLVENT Toluene

MEMBRANE 600 Å cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.1908	0.3258	0.4184				I =	13.89	036	
P	3.00	4.79	6.04				S_{xy}	= 0.035		
Base Line, Po, Cm.	.38	.38	.38				M_w	= 22,209		
π = P-Po	2.62	4.41	5.66							
π/c	13.7317	13.5359	13.5277							



MEMBRANE OSMOMETRY

DATE 8/12/68

GRAPH NO. II

SAMPLE Dimethyl polyurethane #3

OPERATOR Lowry

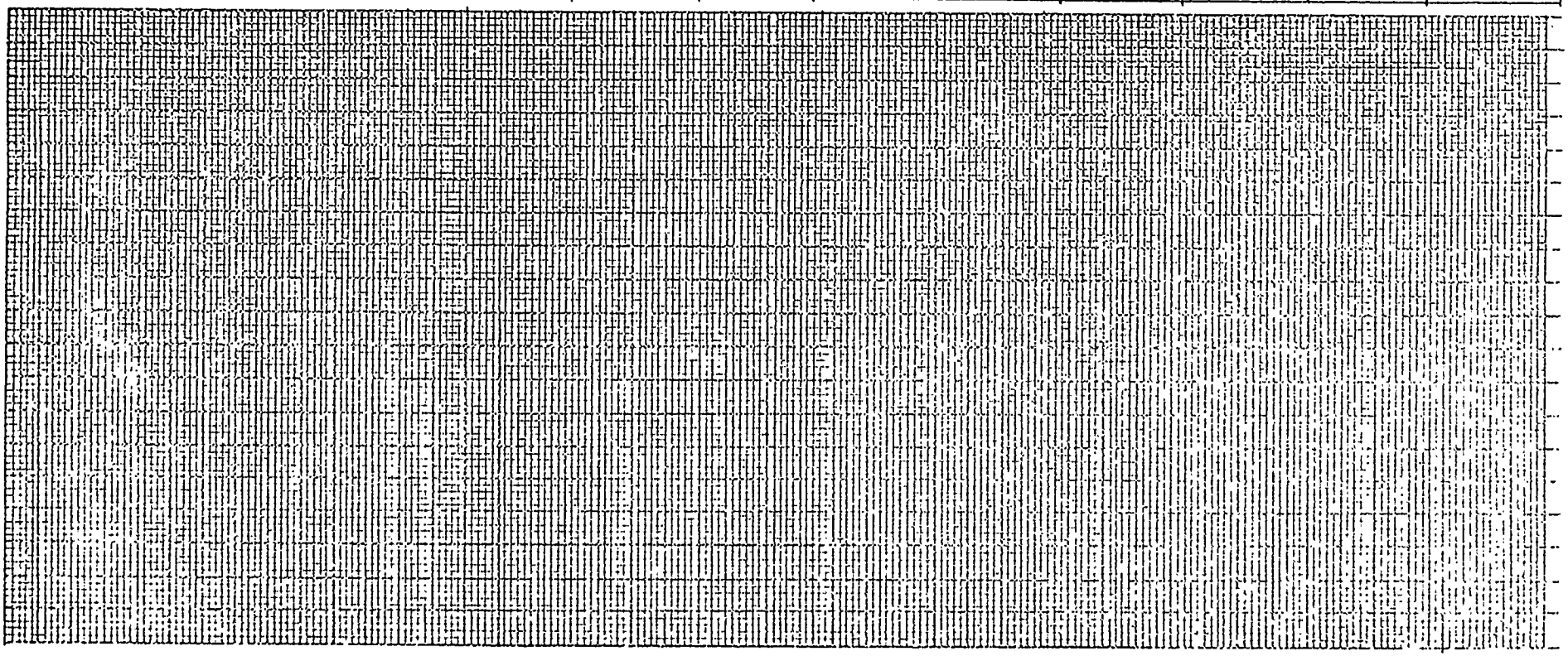
SOLVENT Toluene

MEMBRANE 600 Gel cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.1295	0.1908	0.3258	0.4184			I = 14.31286	
P	2.09	2.96	4.73	5.99			S_{xy} = 0.074	
Base Line, Po, Cm.	.27	.27	.27	.27			M_n = 21,553	
π = P-Po	1.82	2.69	4.46	5.72				
π/c	14.05541	14.0985	13.6894	13.6711				



MEMBRANE OSMOMETRY

DATE 8/12/68

GRAPH NO. III

SAMPLE DMPS-Mixture #3

OPERATOR Lusby

SOLVENT Toluene

MEMBRANE 600 Sel cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.1295	0.1908	0.3258	0.4184			I=	14.3	121	
P	2.13	2.95	4.80	6.04			S_{xy} =	0.06	5	
Base Line, Po, Cm.	.29	.29	.29	.29			M_N =	2,5	55	
π = P-Po	1.84	2.66	4.51	5.75						
π/c	14.2085	13.9413	13.8428	13.7428						

MEMBRANE OSMOMETRY

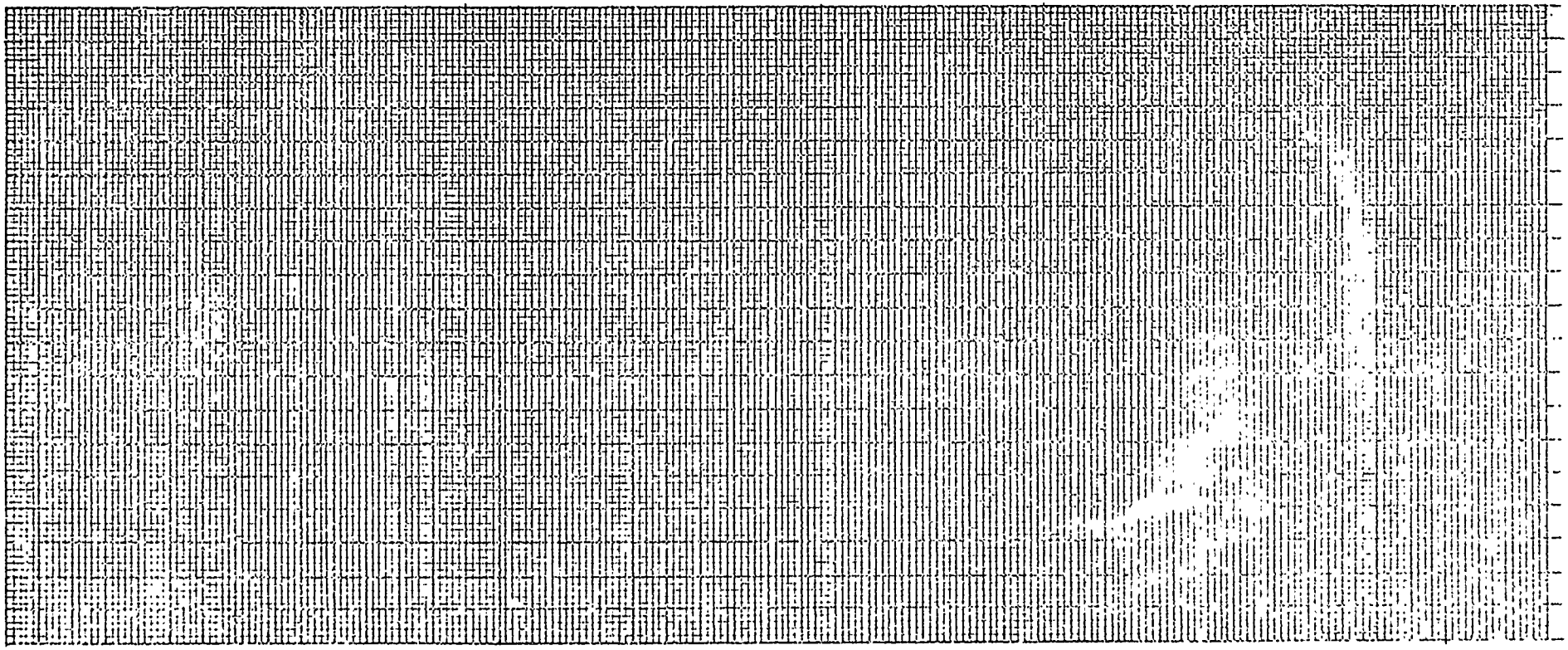
DATE 8/13/68 GRAPH NO. I

SAMPLE DMPS Mw #4 OPERATOR Lutley

SOLVENT Toluene MEMBRANE 600 Sel Cellophane

TEMPERATURE 36.4°C SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2091	0.3270	0.3924				$\bar{I}$ = 14	09508		
P	3.21	4.83	5.65				δ_{xy} = 0.	058		
Base Line, Po, Cm.	.32	.32	.32				M_N = 21,	986		
π = P-Po	2.89	4.51	5.33							
π/c	13.8211	13.720	13.5831							



DG-120

MEMBRANE OSMOMETRY

DATE 8/13/68

GRAPH NO. II

SAMPLE DMPS - Mw # 4

OPERATOR Lurbey

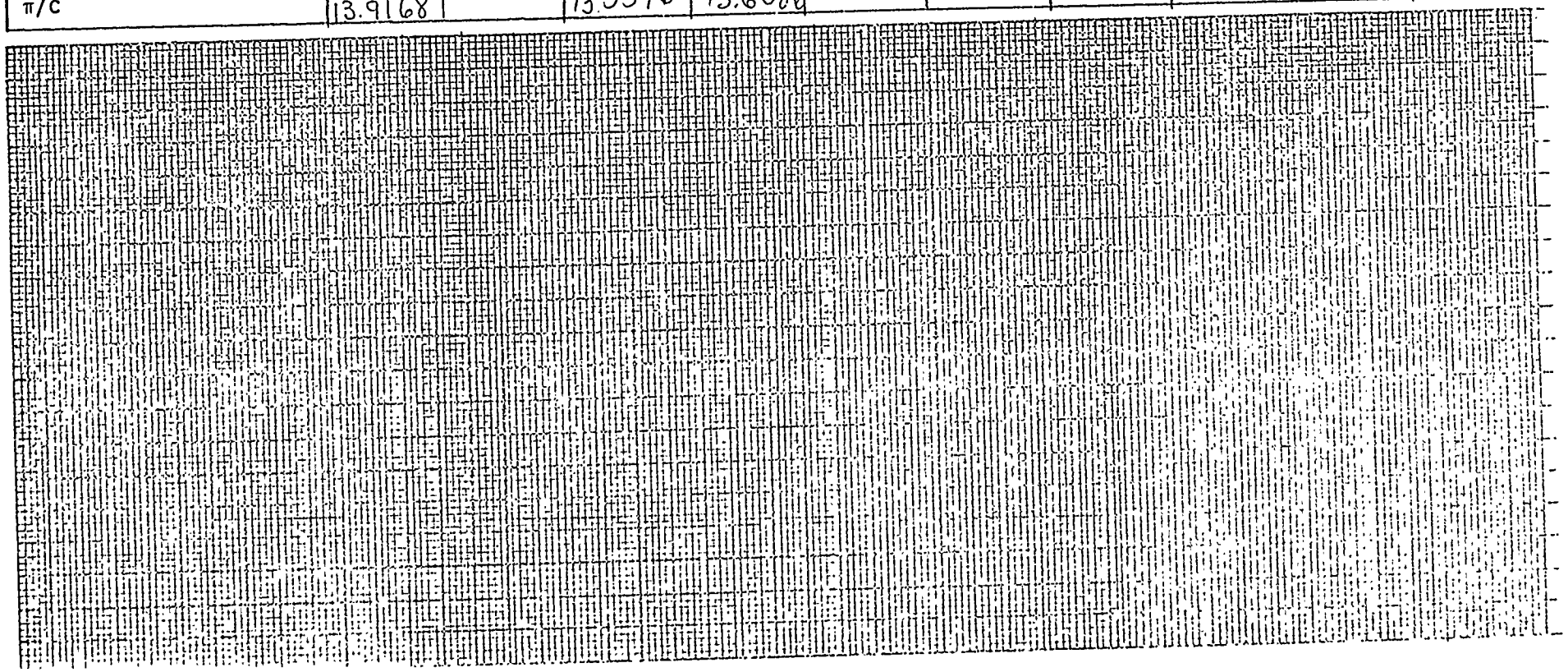
SOLVENT Toluene

MEMBRANE 600 Å Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Concentration @ 100/ML	0.2091	0.3270	0.3924	0.5232			I	= 14.08582		
P	3.28	- - -	5.69	7.49			δx_i	= 0.084		
Base Line, Po, Cm.	.37		.37	.37			M	= 21,900		
π = P-Po	2.91		5.32	7.12						
π/c	13.9168		13.5576	13.6086						



DG-120

MEMBRANE OSMOMETRY

DATE 8/13/68

SAMPLE DMPS - Mix #4

SOLVENT Toluene

TEMPERATURE 36.4°C

GRAPH NO. II

OPERATOR Luthey

MEMBRANE 600 Sel Cellophane

SOLVENT DENSITY 0.8505

Extrapolated

57.90977622

Concentration @ 100/ML	0.2091	0.3270	0.3924	0.5232						
P	3.28	---	5.77	7.56			I =	14.02211		-.571405
Base Line, Po, Cm.	.37		.37	.37			S_{xy} =	0.025		
π = P-Po	2.91		5.40	7.19			M_N =	22.200		
π/c	13.9168		15.7615	13.7429						

MEMBRANE OSMOMETRY

DATE 8/13/68

GRAPH NO. • P III

SAMPLE DMPS Mw-#4

OPERATOR Luthey

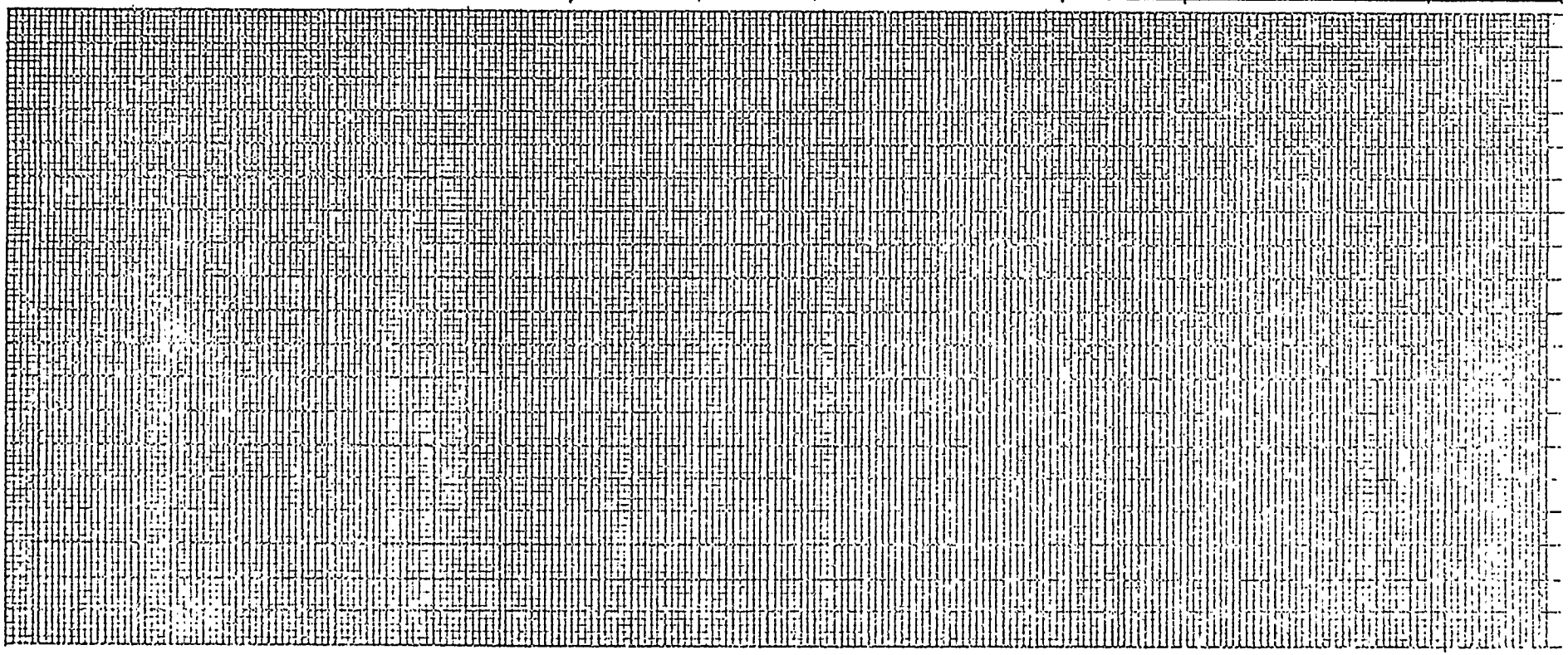
SOLVENT Toluene

MEMBRANE 600 Ge.P Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 08505

Concentration @ 100/ML	0.2091	0.3270	0.3924	0.5232						
P	3.29	4.88	[illegible]	7.47			$I = 14.2780$			
Base Line, Po, Cm.	.36	.36		.36			$S_{xy} = 0.014$			
π = P-Po	2.93	4.52		7.11			$M_n = 21,606$			
π/c	14.0124	13.8226		13.5894						



MEMBRANE OSMOMETRY

DATE 8/13/68

GRAPH NO. R III

SAMPLE DAPS #4

OPERATOR Lutley

SOLVENT Toluene

MEMBRANE 600 Sel Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

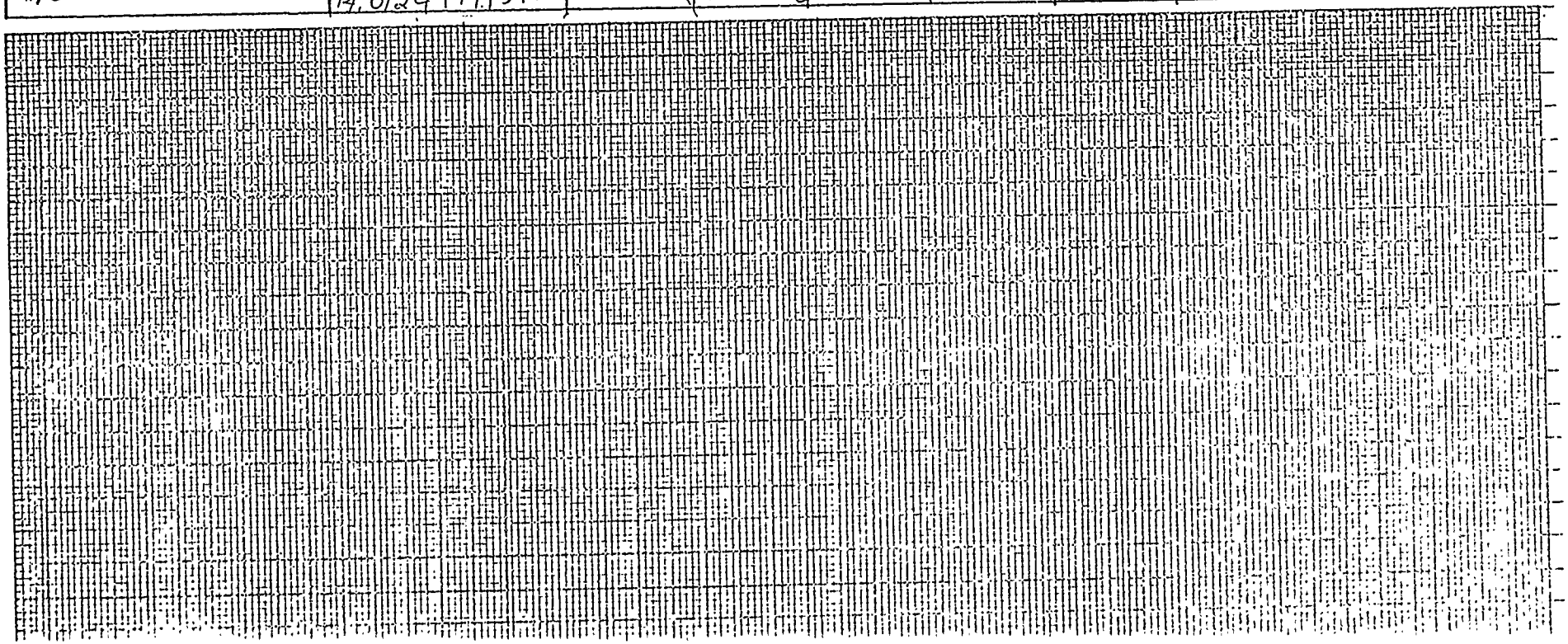
Extrapolated

Concentration @ 100/ML	0.2091	0.3270	0.3924	0.5232
P	3.29	4.99	6.01	7.65
Base Line, Po, Cm.	.36	.36		.36
π = P-Po	2.93	4.63		7.29
π/c	14.0124	14.1590		13.9335

$\bar{I}$ = 14.15592

S_{xy} = 0.0182

M_n = 21,792



MEMBRANE OSMOMETRY

DATE 8/8/68

GRAPH NO. III

SAMPLE THF #2 DMPS

OPERATOR Lukey

SOLVENT Toluene

MEMBRANE 600 Hel Cellophane

TEMPERATURE 36.4°C

SOLVENT DENSITY 0.8505

Extrapolated

Concentration @ 100/ML	.2013	0.3288	0.4305	0.5168						
P	3.09	5.11	6.48	7.90			S_{xy} =	0.22		
Base Line, Po, Cm.	.40	.40	.40	.40			M_N =	23,913		
π = P-Po	2.69	4.71	6.08	7.50						
π/c	13.3631	14.3248	14.1231	14.5124						

I = 12.9 0046 2.1

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