MASTER

Conf-

(1, d)

CONF-117-9

Measurement
of
Dynamic Surface Tension
in Bubbling Systems

John B. Roll*
John E. Myers

School of Chemical Engineering
Purdue University

1963

* Present address: Division of Reactor Development
United Stated Atomic Energy Commission
Washington 25, D. C.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The following pages are an exact representation of what is in the original document folder.

Measurement of Dynamic Surface Tension in Bubbling Systems

John B. Roll* and John E. Myers

School of Chemical Engineering, Purdue University

ABSTRACT

The static and dynamic surface tension has been measured for
aqueous solutions of eleven surface active agents for the purpose
of studying the effect of surface tension upon boiling heat trans-
fer. The surfactants have been chosen from the Tween, Aerosol, and
Hyonic series. Dynamic surface tension, at $T = 90^{\circ}C$, was investigated
by observing the volume and frequency for air bubbles forming from a
submerged orifice. Static surface tension, at $T = 100^{\circ}C$, was measured
using a duNouy tensiometer. In all cases, the dynamic surface tension
for solutions of these surface active agents was less than the value
for pure water, greater than the static value for the same concentra-
tion, and was a smoothly decreasing function of concentration.

* Present address: Division of Reactor Development
United States Atomic Energy Commission
Washington 25, D. C.

Measurement of Dynamic Surface Tension in Bubbling Systems

John B. Roll* and John E. Myers

School of Chemical Engineering, Purdue University

Early in the course of an investigation into the effects of
surface tension upon boiling heat transfer (4) it was apparent that
a method of determining, or at least characterizing, the effective
surface tension of a surfactant solution under non-equilibrium con-
ditions was required. Methods of measuring dynamic (non-equilibrium)
surface tension are discussed by Schwartz and Perry (5) and include
the falling drop, the pulsating jet, and the impinging jet methods.
While these methods do measure a dynamic surface tension, it was
felt that in this case a device as similar to boiling systems as
possible was required.

Apparatus

The apparatus for determining dynamic surface tension (figure 1)
consisted of a gas train terminating at a brass orifice of known
diameter. Volumetric flow control was achieved using an air valve
with a constant effluent pressure. The flow rate was determined
by noting the time required for a soap bubble to pass between two
marks on a volumetric buret - this device is known as a "soap-bubble
flow-meter." The pressure in the buret was determined with a mer-
cury manometer. A 130 cm length of nominal $\frac{1}{2}$ mm ID glass capillary
was placed directly behind the orifice to maintain constant flow
rate. The orifice was drilled in a piece of brass bar-stock, $\frac{1}{2}$"

* Present address: Division of Reactor Development
United States Atomic Energy Commission
Washington 25, D. C.

OD x 1-1/8" long; the 1/16" (0.159 cm) hole was drilled at the axis. The surface of the orifice was polished with "O" grade emer; paper. Bubble frequency was determined using a General Radio Stroboscope. The vessel containing the test liquid was a one gallon glass jar. It was supported inside a constant temperature oil bath capable of maintaining a temperature of $90^\circ \pm 1^\circ C$ within the test jar. A mercury thermometer gave this temperature.

Operating procedure consisted of filling the jar with $2\frac{1}{2}$ liters of water and an appropriate amount of surfactant and adjusting the oil bath heaters until the desired temperature was reached by the liquid in the jar. Data points were taken by noting: bubble frequency, gas flow rate, buret pressure, and liquid temperature.

Calculation Procedure

The data consisted of:

T   bath temperature $(^\circ C)$

ΔP pressure in the gas buret (mm mercury, gauge)

q'   gas rate in gas buret, at pressure and temperature of buret (cm^3/sec)

f   bubble frequency (bubbles/minute)

From these data q, the volumetric flow rate through the orifice, was calculated:

$$q = q' \left(\frac{760 + \Delta P}{760} \right) \left(\frac{273 + T}{273 + 25} \right) \qquad (1)$$

Equations for the volume of air in the bubble and the diameter of
an equivalent spherical bubble are:

$$V = \frac{60_q}{f}$$

(2)

and

$$D = \left(\frac{6 \alpha \cdot V}{\pi} \right)^{\frac{1}{3}}$$

(3)

where α is a constant factor to correct for water vapor in the
bubble as a result of evaporation at the bubble surface during for-
mation. The temperature correction involves the assumption that the
gas in the buret was at $25^\circ C$ and that the bubble was fed gas at the
bath temperature. It can be shown that under conditions of this
experiment, the latter assumption was justified.

Equations

Hayes, et al, (1) and Hughes, et al, (2) have analyzed the
forces acting on a growing bubble. Their results can be expressed
in the following equation:

$$\alpha V \Delta\rho \, g \, (1-\psi) = \pi D_0 \sigma \left(1 - \frac{D_0}{D} \right) - \psi$$

(4)

where the quantity ψ is related to the drag forces exerted by the
liquid on the bubble and is defined as:

$$\psi = \left(\frac{3\rho_\ell}{4\Delta\rho} \right) \left(\frac{g^2 \alpha^2}{\pi D^5 g} \right) \left(C_\alpha - \frac{16\pi}{3} \right)$$

(5)

The quantity ψ is defined as:

$$\psi = \frac{4 \eta^2 \rho_i}{\pi} \frac{\alpha}{D_0^2} \left[1 - \frac{c'}{12} \left(\frac{D_0}{D} \right)^2 \right] \qquad (6)$$

This latter expression contains terms related to the momentum of the gas.

The application of equation (4) was accomplished in two steps. The first involved taking data with pure water at various temperatures and evaluation of the unknown factors in equation (4). The second involved taking data with surfactant solutions and, using the results of step one, to evaluate the apparent or dynamic surface tension.

For step one, data were taken at temperatures of 30°, 50°, 70°, and 90°C over the frequency range 1000 - 1900 bubbles per minute in 100 bubble per minute increments. Over this range ψ was negligible when compared to the other terms in equation (4) and was accordingly discarded. Equation (4) was then written:

$$(1 - \psi) = \frac{\pi D_0 \sigma \left(1 - \frac{D_0}{D} \right)}{\alpha V \Delta \rho g} \qquad (7)$$

The quantity $(1 - \psi)$ was correlated with experimental data for pure water using as parameters the dimensionless groups:

$$N_{Re} = \frac{D u \rho_i}{\mu_i} = \frac{\alpha g \rho_i}{\pi D \mu_i} \qquad (8)$$

and

$$N_\sigma = \frac{\sigma \rho_i D_0}{\mu_i^2} \qquad (9)$$

The group N_σ was used by Hughes et al, (2) as a parameter (along with N_{Re}) to correlate measurements of drag coefficients for bubbles. The quantity N_σ is known as the Ohnesorge number and has been used to characterize the breakup of liquid jets (3). It is readily seen that it is equal to the square of the Reynolds number divided by the Weber number ($\rho_\ell u^2 D_o / \sigma$).

The data for pure water are shown in figure 2 as $(1 - \psi)$ versus N_{Re} at various values of N_σ . Values for $(1 - \psi)$ were calculated using equation (7). Since the data used were for a pure liquid, the values of σ were the static values which were of course identical with the dynamic values for this special case. From step 2 it was found that the data for determing dynamic surface tension fell within the range: $240 < N_{Re} < 550$; $3.54 < (N_\sigma \times 10^{-5}) < 9.28$. Accordingly, data in these ranges obtained in step 1 were correlated using a multiple, linear regression technique. The equation obtained was:

$$(1 - \psi) = 0.6755 \, N_{Re}^{-.778} \, N_\sigma^{.272} \tag{10}$$

Equation (10) was used to eliminate $(1 - \psi)$ from equation (7), the results being:

$$\sigma = \left[\frac{444.9 \, \rho_\ell^{.994} \, \mu_\ell^{.233}}{D_o^{.728}} \frac{D^{2.09}}{f^{.778}(D - D_o)} \right] \tag{11}$$

Step 2 involved taking bubble volume data with four concentrations of each of eleven surfactants at $T = 90°C$. These data were plotted as V versus f, and the volumes at $f = 1800$ bubbles/min arbitrarily used

to determine a characteristic dynamic surface tension.

Evaluation of α

A Wollensak Fastex camera was used to take four sets of high speed, motion picture photographs. Two of these sequences were with water (f = 1500 and 1800 bubbles per minute and T = 90°) and two with surfactant solutions (f = 1500 and 1800 and T = 90°). By projecting the resulting film strips frame by frame, it was possible to compare actual growth rate and final volume to the values determined assuming the bubble contained only dry air. This procedure yielded a value: α = 2.1 with a standard deviation of 0.15. On this basis α was assumed constant for the conditions investigated.

Static Surface Tension

To provide a comparison, the static surface tension, at temperatures ranging from room temperature to 100°C, was measured with a duNouy Tensiometer for the eleven surfactants under consideration. The solution was contained in a 250 ml boiling flask. It was heated with an electric mantle, controlled by a small Variac. Temperatures were measured with a copper-constantan thermocouple contained in a glass well. By careful adjustment of the Variac, it was possible to maintain the solution at constant temperature for sufficient time to read the Tensiometer. At the higher temperature determinations, it was necessary to adjust the Tensiometer between readings to compensate for water which had condensed on the Tensiometer ring stirrup and arm.

Results

Eleven surfactants (see table I) were considered in this work. The results are plotted as observed dynamic surface tension at $f = 1800$ and $T = 90°$, denoted by σ_d, and as measured static surface tension at $T = 25°$ and $100°$, denoted by σ_{25} and σ_{100} respectively, versus concentration. In all cases the following behavior was observed: 1) σ_d is less than the surface tension for pure water but greater than the corresponding static value; 2) σ_d is a smoothly decreasing function of concentration, seeming to approach asymptotically the equilibrium value.

Acknowledgements

Nomenclature

C_d drag coefficient

D diameter of sphere of volume equivalent to bubble (cm)

D_o diameter of orifice (cm)

f bubble frequency (min^{-1})

ΔP pressure in gas buret (mm mercury)

q volumetric gas flow rate at T and P at orifice (cm^3/sec)

q' volumetric gas flow rate at T and P of gas buret (cm^3/sec)

T temperature (°C)

u bubble velocity (cm/sec)

V volume of air in bubble (cm^3)

ψ defined in equation (5)

φ defined in equation (6)

α $\dfrac{\text{volume of bubble}}{\text{volume of air in bubble}}$

η that fraction of the displaced mass of liquid which acts as an acceleration drag force

ρ_i liquid density (gm/cm^3)

σ_d dynamic surface tension at $f = 1800$ (dynes/cm)

σ_{25} static surface tension at $T = 25°$ (dynes/cm)

σ_{100} static surface tension at $T = 100°$ (dynes/cm)

μ_i liquid viscosity (gm/cm sec)

Literature

1. Hayes, W. B., Hardy, B. W., and Holland, C. D., _AIChEJ_, _5_, 319 (1959).

2. Hughes, R. R., Handlos, A. E., Evans, H. D., and Maycock, R. L., _CEP_, _51_, 557, (1955).

3. Miesse, C. C., Ind. Eng. Chem. _47_, 1690 (1955).

4. Roll, J. B., "The Effect of Surface Tension of Boiling Heat Transfer", Ph. D. Thesis, Purdue University, August 1962.

5. Schwartz, A. M., and Perry, J. W., "Surface Active Agents," Vol. I, Interscience Publishers, Inc., New York, (1949).

List of Figures

FIGURE I Dynamic Surface Tension Apparatus

LINES FROM
CORRELATION EQ. 14

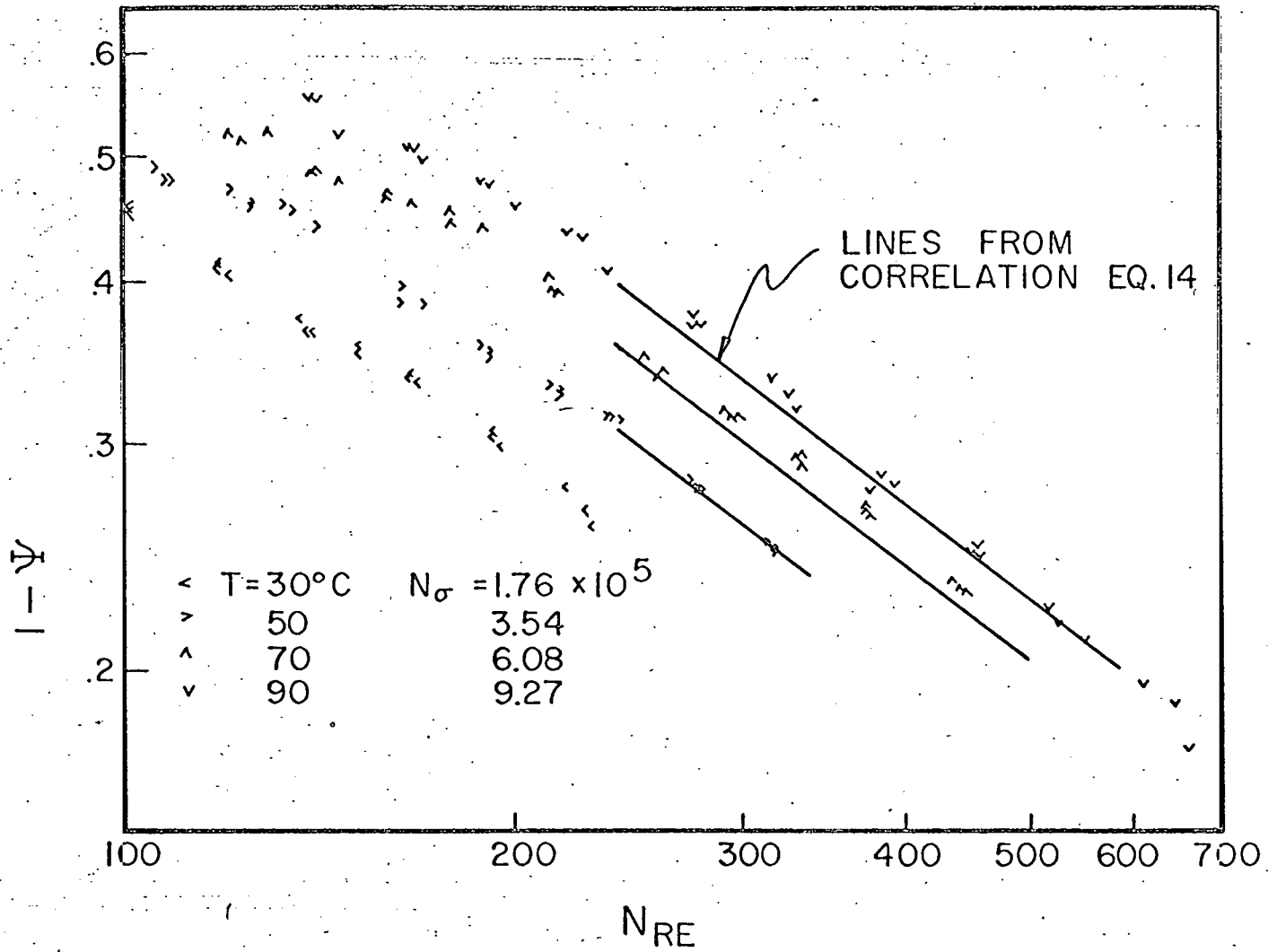| < | T=30°C | N_σ =1.76 ×10^5 |
>	50	3.54
^	70	6.08
v	90	9.27

$1-\Psi$

N_{RE}

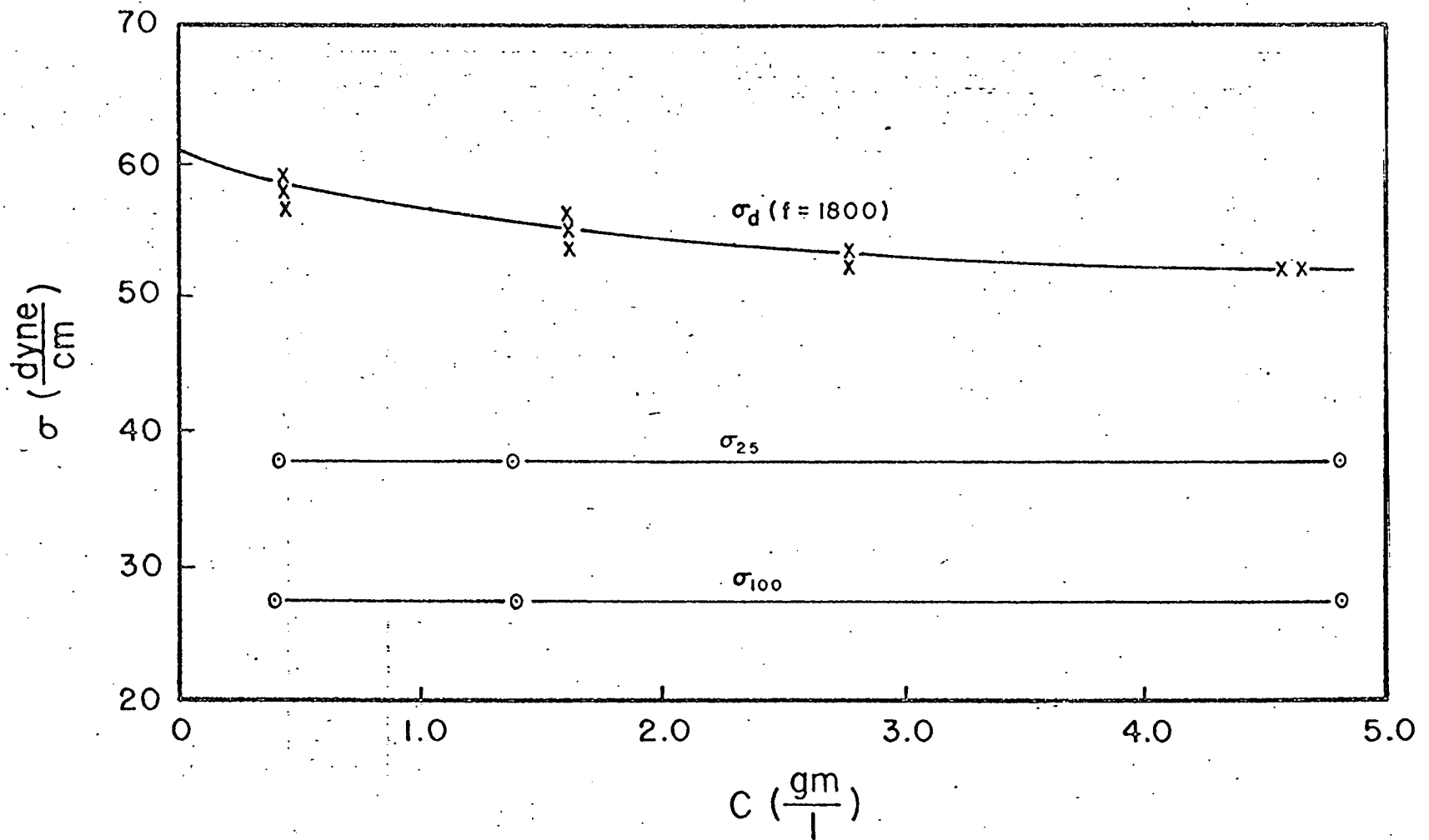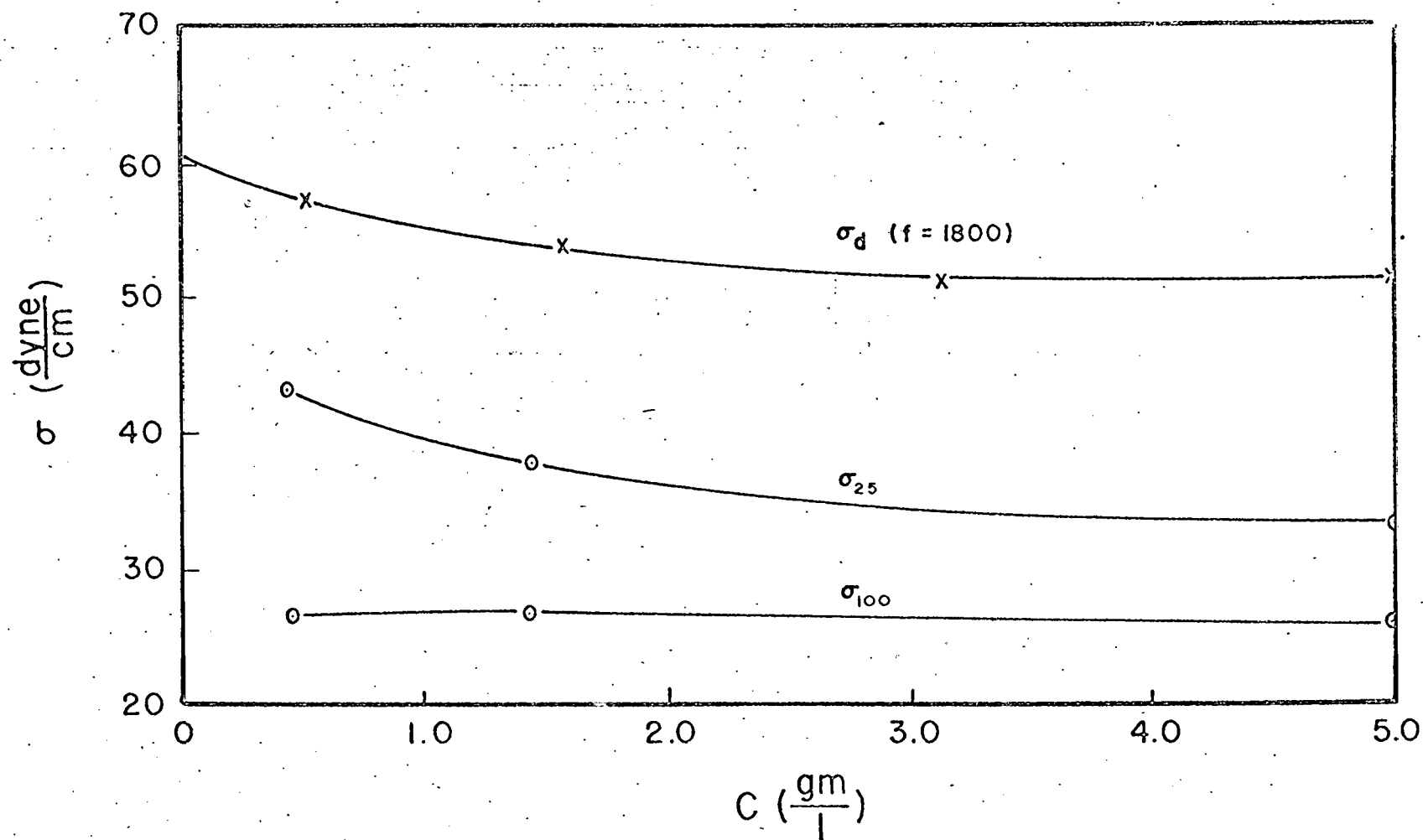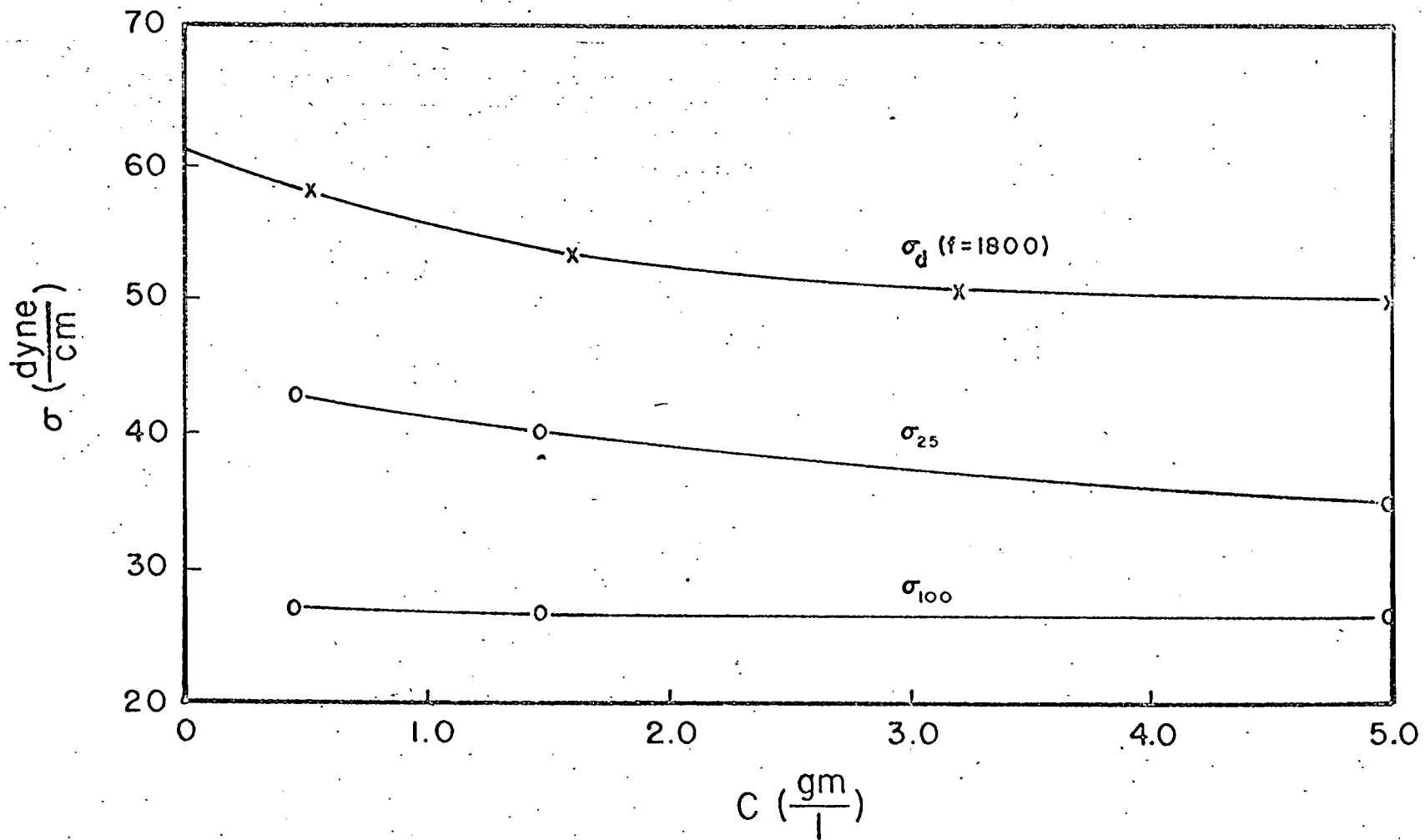FIGURE 23 $\overline{1-\Psi}$ Versus N_{RE} For Various N_σ

FIGURE 3/7   Surface Tension Versus Concentration
Tween 80

FIGURE 4   Surface Tension Versus Concentration
Tween 60
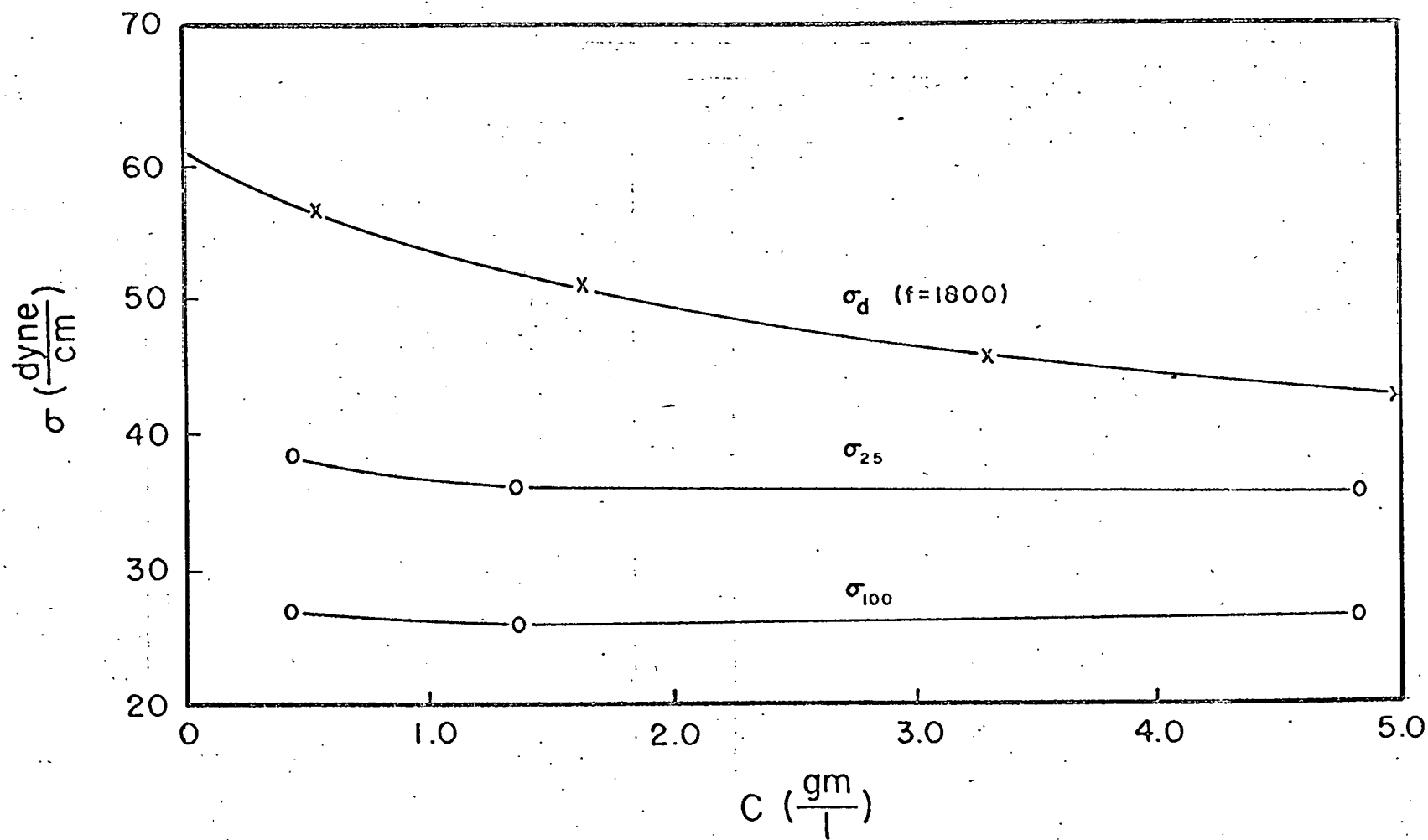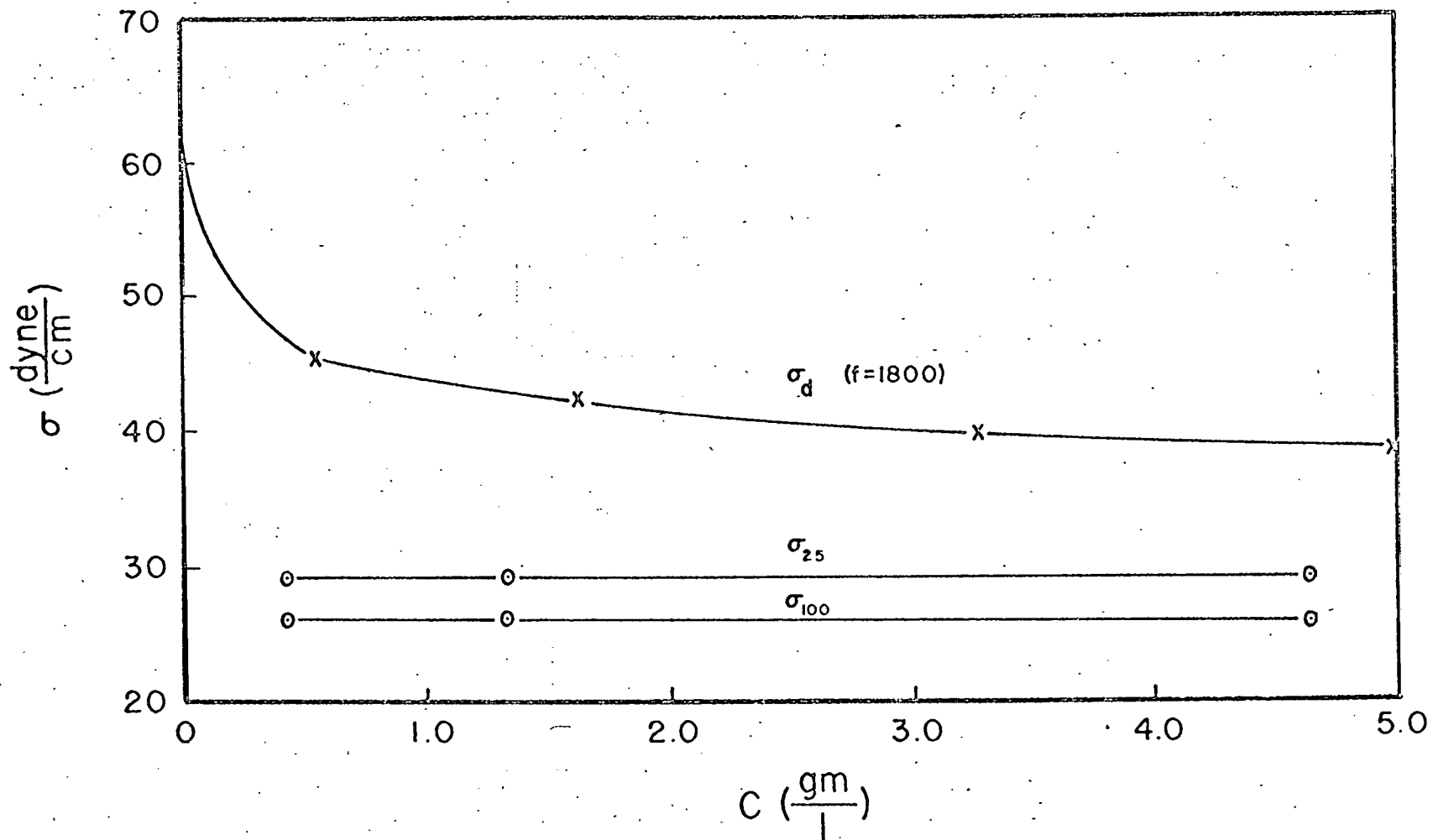
FIGURE 5 Surface Tension Versus Concentration Tween 40

FIGURE 16   Surface Tension Versus Concentration
Tween 20

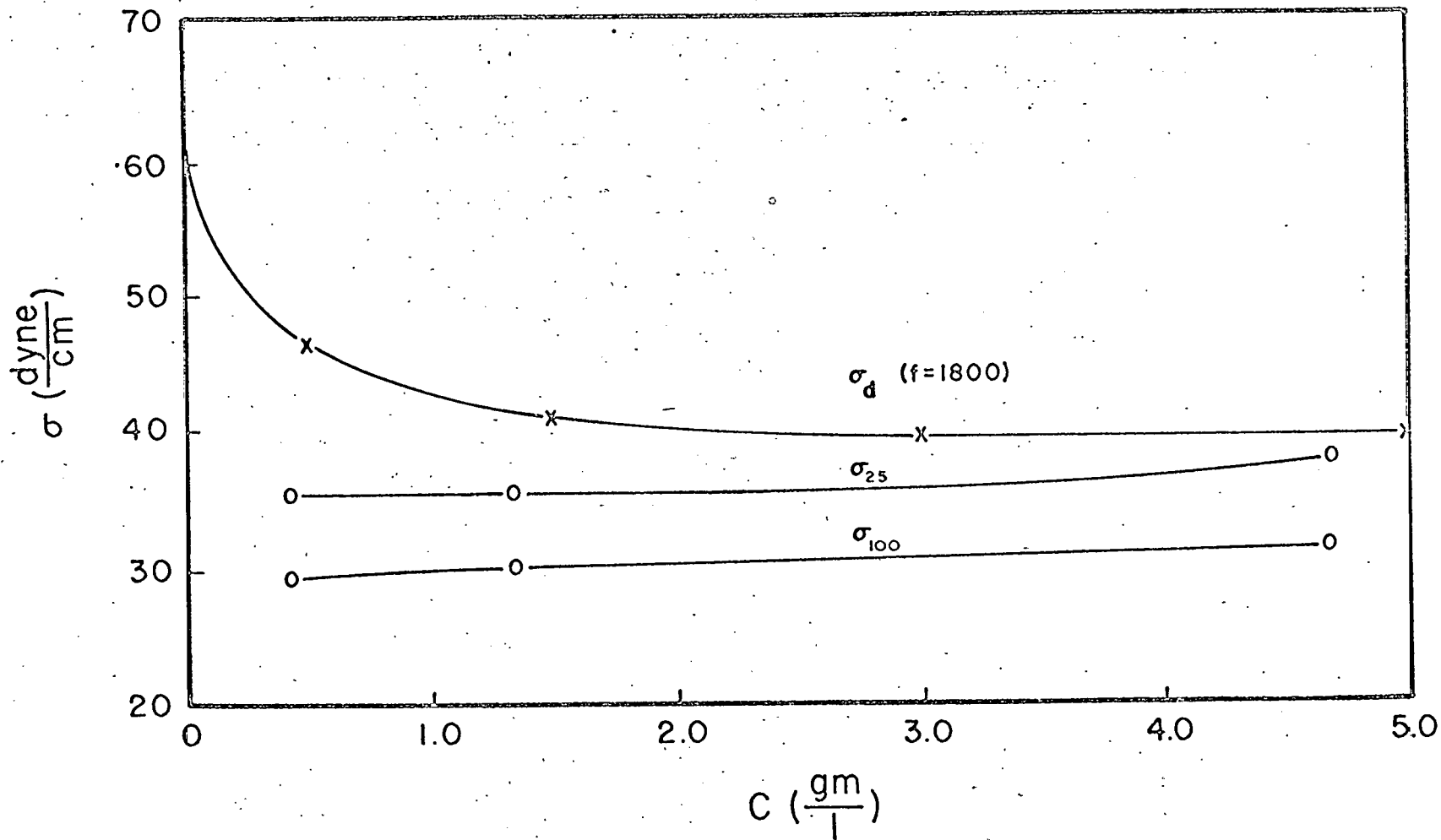FIGURE 7 Surface Tension Versus Concentration
Hyonic PE 100

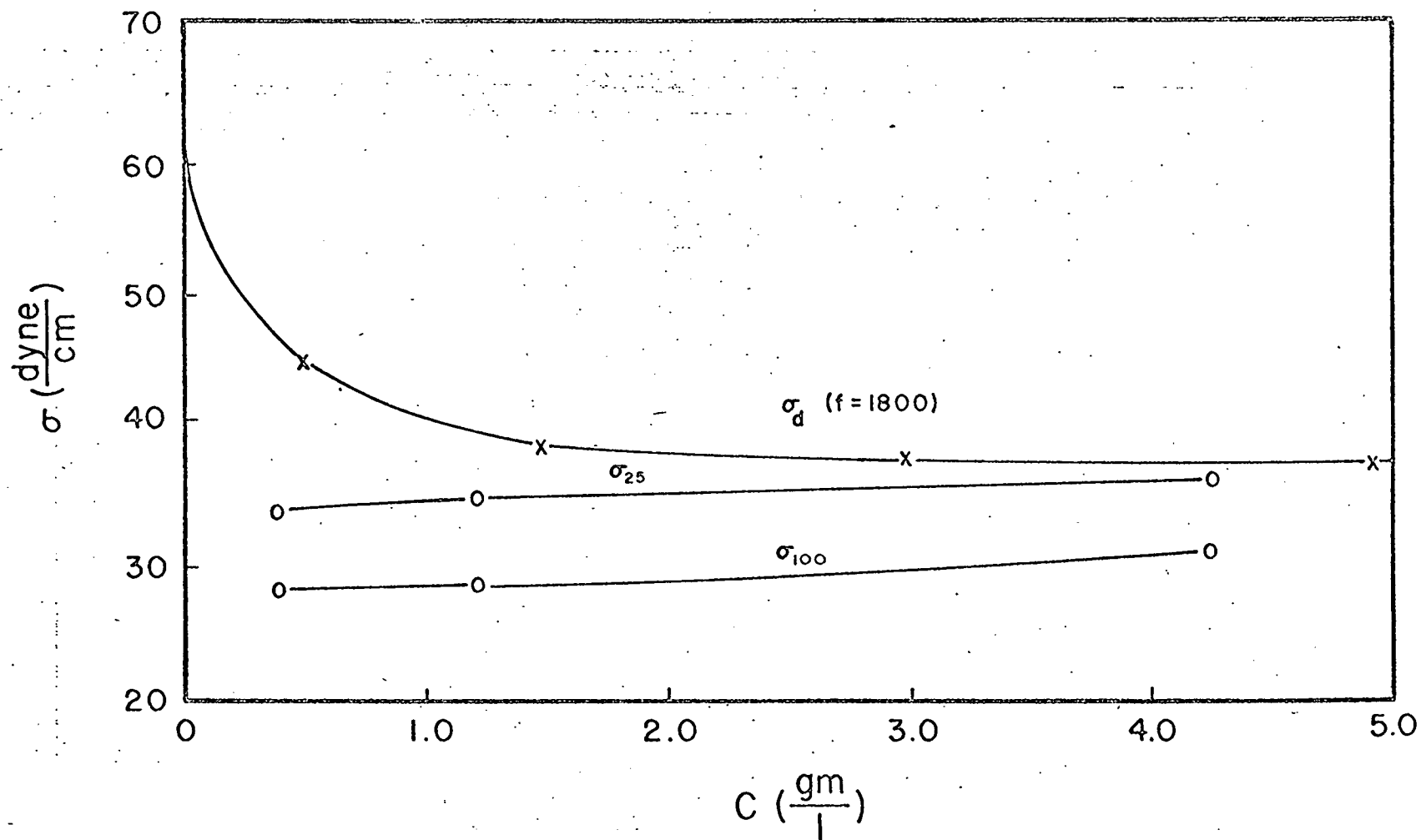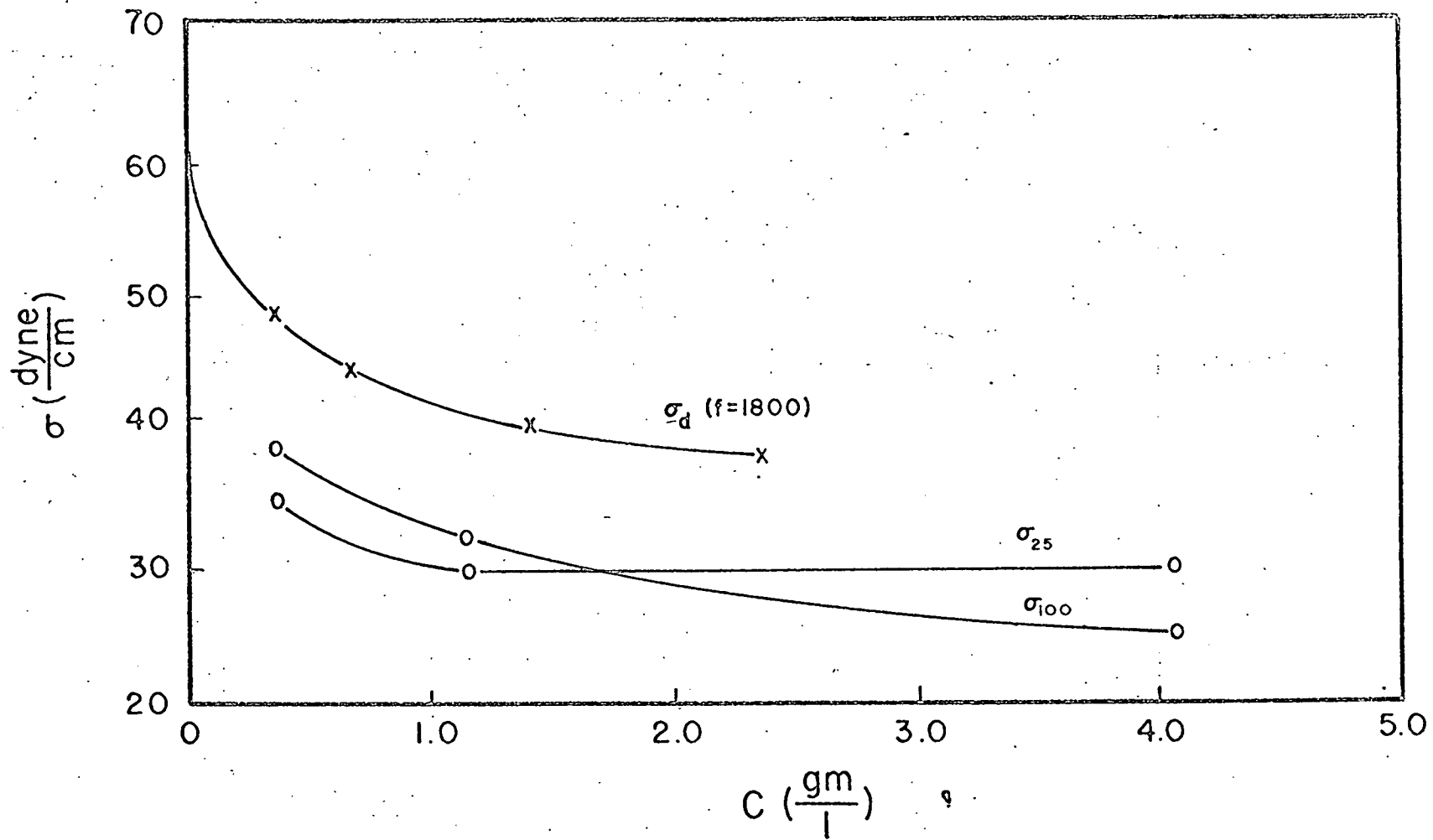FIGURE 18 Surface Tension Versus Concentration
Hyonic PE 200

FIGURE 9 Surface Tension Versus Concentration
Hyonic PE 300

33

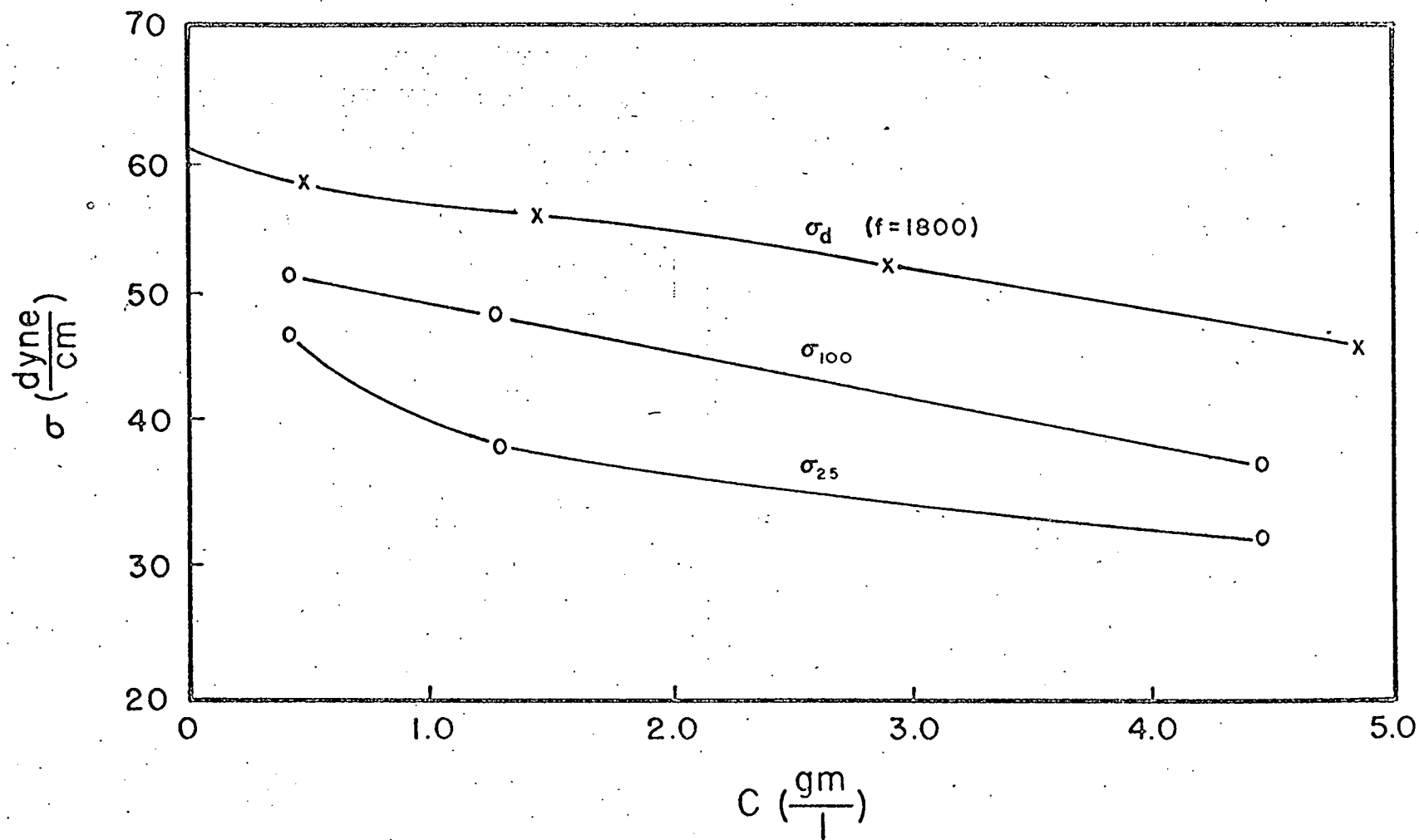FIGURE 10 Surface Tension Versus Concentration Aerosol OT (75% AQ)
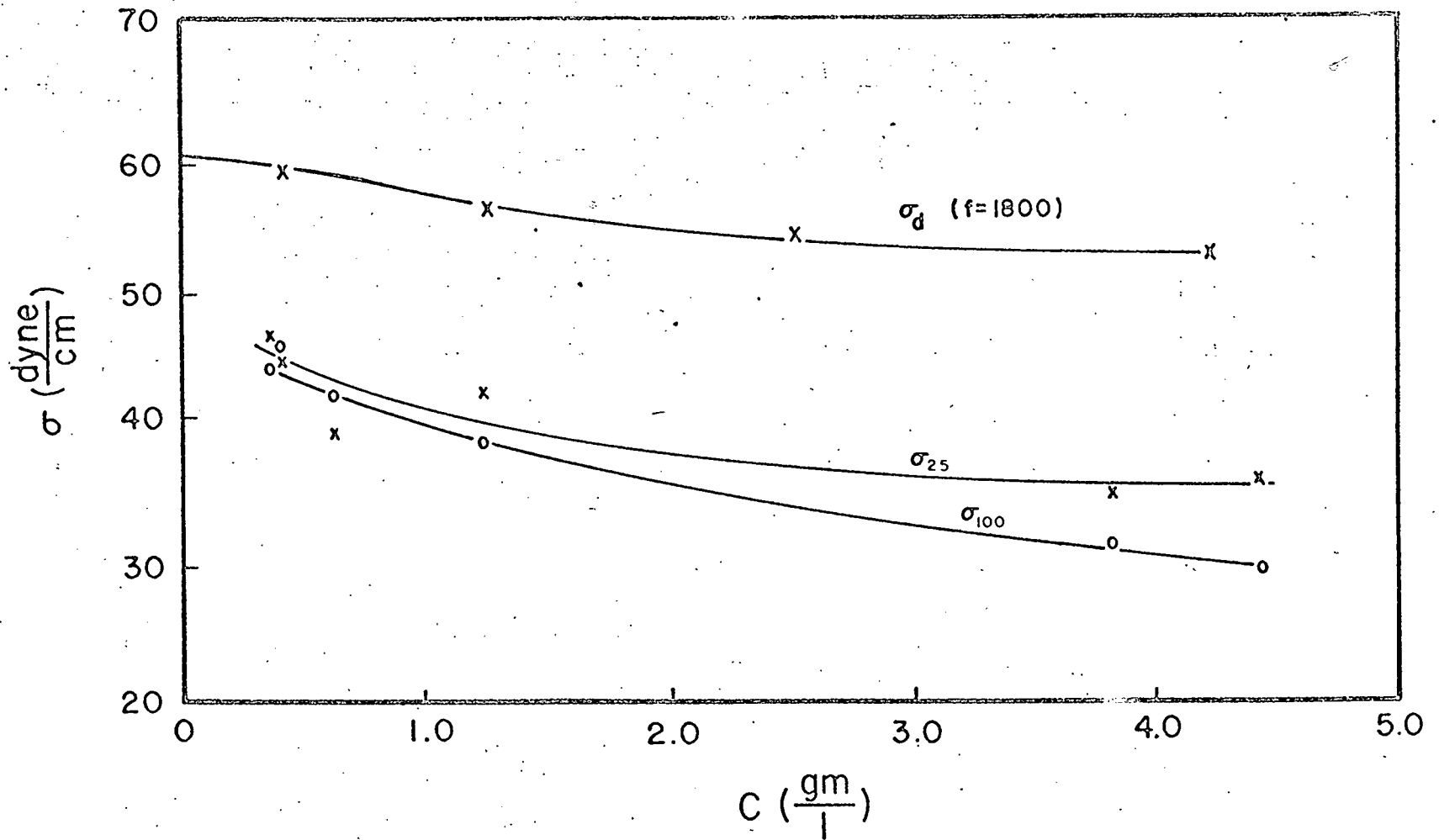
FIGURE 15 Surface Tension Versus Concentration
Aerosol AY
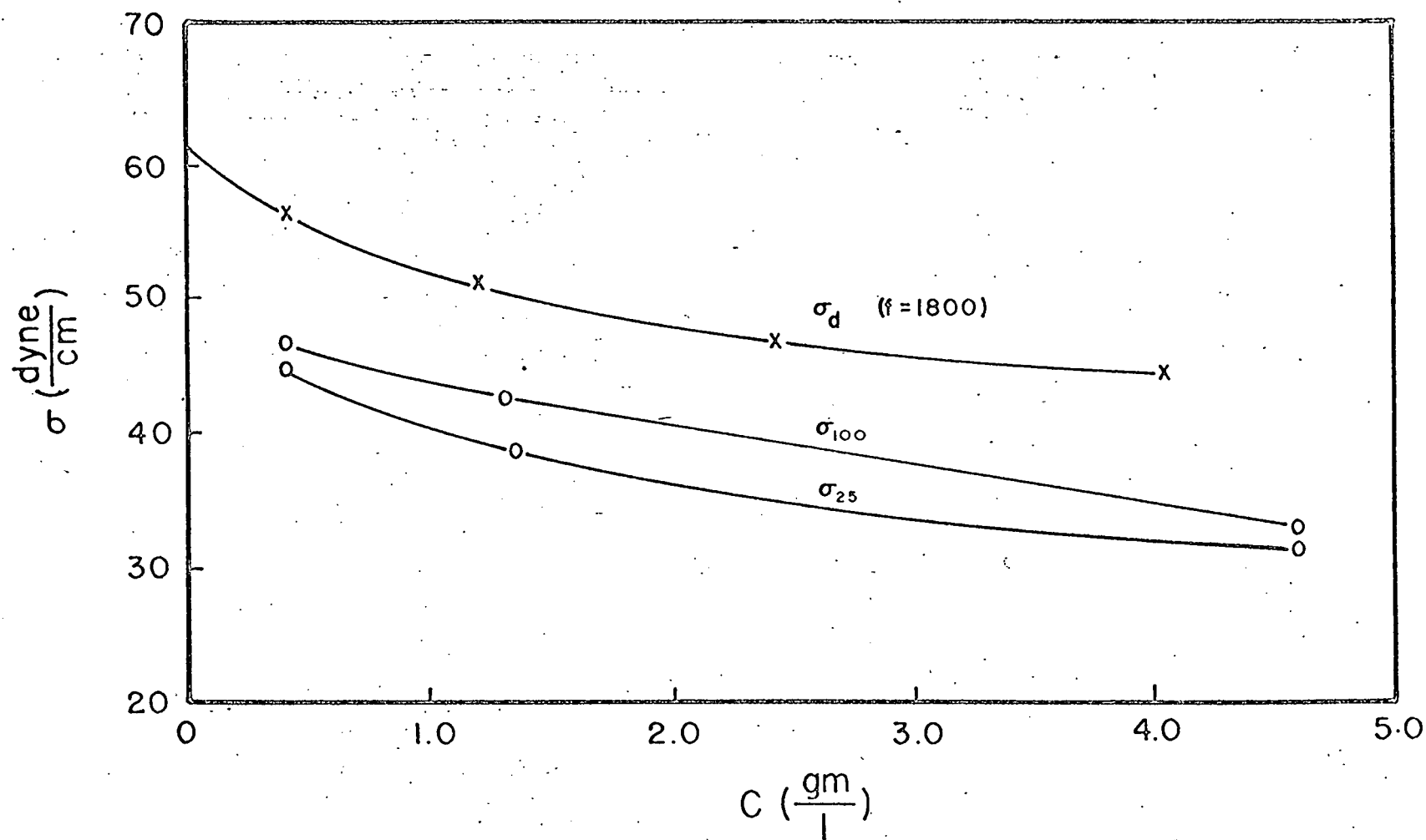
FIGURE 12 Surface Tension Versus Concentration
Aerosol IB

FIGURE 13 17 Surface Tension Versus Concentration
Aerosol MA

Table 16

Properties of Surfactants

Trade Name	Chemical Name	Mole Wt.	Sp. Gr.	Manufacturer
Aerosol AY	Diamyl Sodium Sulfosuccinate	360	–	American Cyanamid Co.
Aerosol IB	Diisobutyl Sodium Sulfosuccinate	332	–	"
Aerosol MA	Dihexyl Sodium Sulfosuccinate	388	–	"
Aerosol OT	Dioctyl Sodium Sulfosuccinate	445	–	"
Tween 20	Polyethylene Sorbitan Monolaurate	1226	1.10	Atlas Chemical Industries
Tween 40	Polyethylene Sorbitan Monopalmitate	1282	1.08	"
Tween 60	Polyethylene Sorbitan Monostearate	1310	1.10	"
Tween 80	Polyethylene Sorbitan Monooleate	1308	1.08	"
Hyonic PE-100	Polyethylene (10) Octyl Phenol Condensate	536	1.078	Nopco Chemical Company
Hyonic PE-200	Polyethylene (20) Octyl Phenol Condensate	856	1.117	"
Hyonic PE-300	Polyethylene (30) Octyl Phenol Condensate	1176	1.159	"