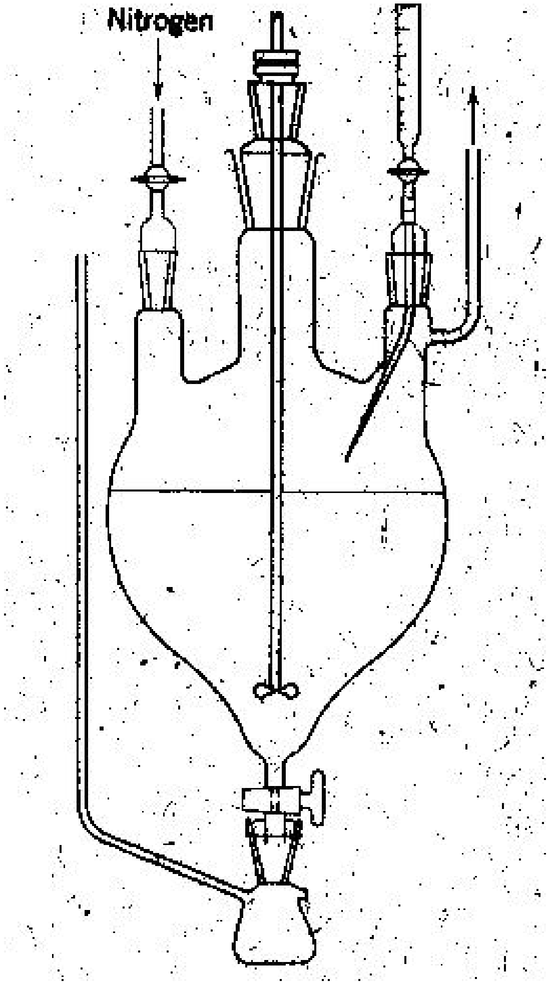
FRACIONAMENTO POR SOLUBILIDADE



- Solução polimérica diluída
- Controle de temperatura
- Controle de atmosfera
- Adição de não-solvente
- Aquecimento/resfriamento
- Precipitação
- Isolamento do precipitado
- Repetição das operações

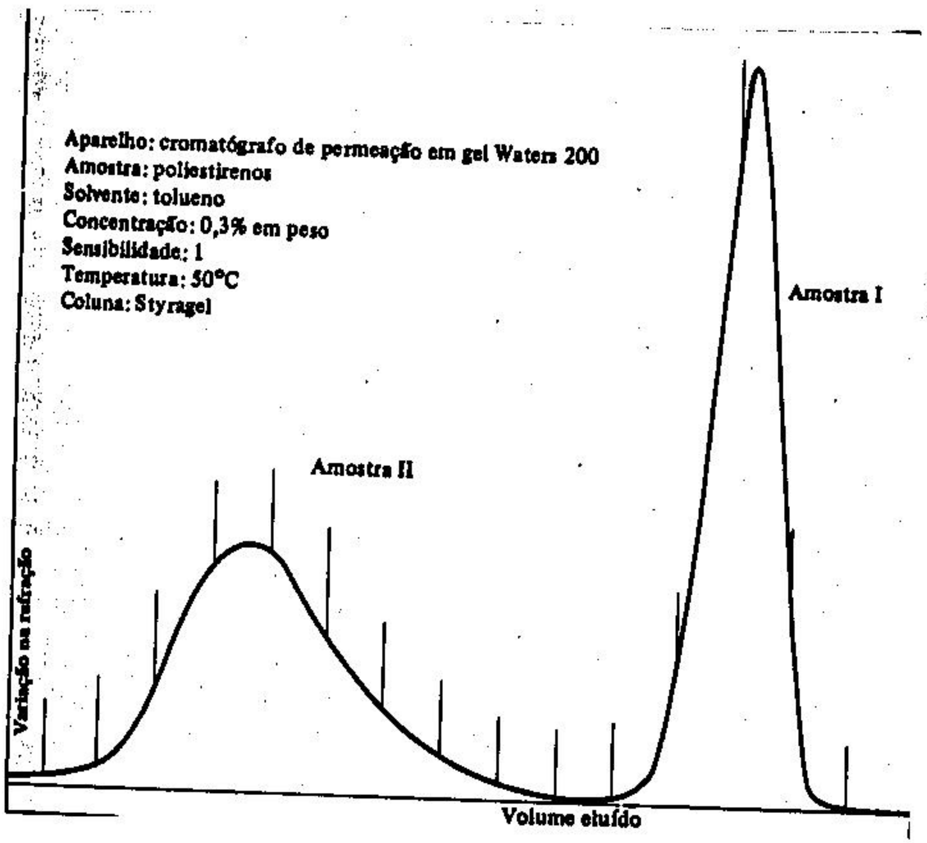
DETERMINAÇÃO DE MASSAS MOLARES MÉDIAS

- MASSA MOLECULAR MÉDIA
  - NUMÉRICA: $(\overline{M}_n) = \dfrac{\sum n_i M_i}{\sum n_i}$
  - PONDERAL: $(\overline{M}_w) = \dfrac{\sum n_i M_i^2}{\sum n_i M_i}$
  - VISCOSIMÉTRICA: $(\overline{M}_v) = (\sum n_i M_i^{1+a})^{1/a} / \sum n_i M_i$

- DISTRIBUIÇÃO DE MASSA MOLECULAR

DISTRIBUIÇÃO DE MASSAS MOLARES

$Ip = Mw / Mn$



VISCOSIDADE EM SOLUÇÃO DILUÍDA

•viscosidade relativa: $$\eta_r = \frac{\eta}{\eta_0}$$

•viscosidade específica: $$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

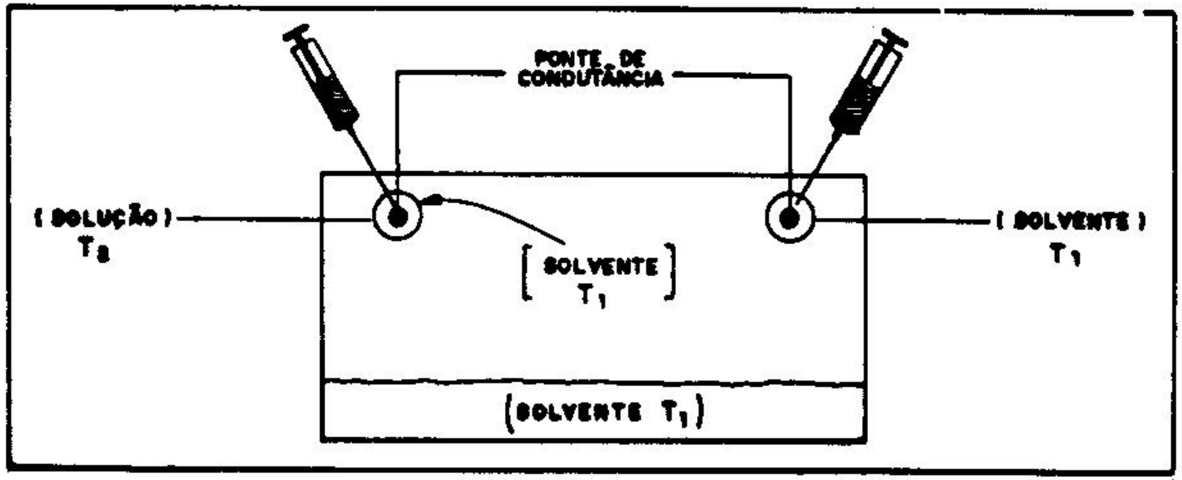
•viscosidade reduzida: $$\eta_{red} = \frac{\eta_{sp}}{C}$$

•Huggins $$\frac{\eta_{sp}}{C_p} = [\eta] + k_H.[\eta]^2.C_p$$

$$[\eta] = K'\overline{M}_v^{\alpha}$$

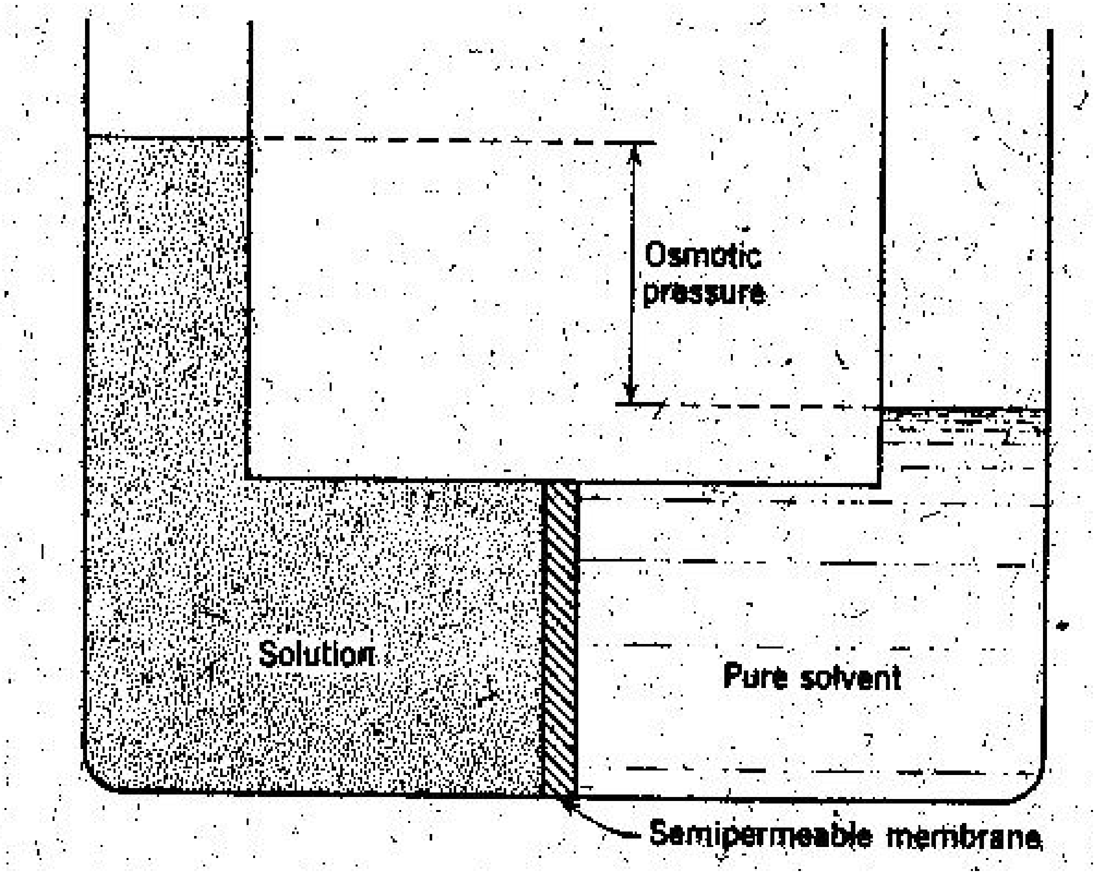
$$\overline{M_v} = \frac{(\sum n_i M^{1+a})^{1/a}}{\sum n_i M_i}$$

OSMOMETRIA EM FASE VAPOR/TONOMETRIA



- **LIMITAÇÕES:**
- $Mn \leq 40000$ g/mol
- Solubilidade
- Perdas de calor
- Precisão
- Reprodutibilidade

OSMOMETRIA DE MEMBRANA



- **LIMITAÇÕES**
- Mn>50000 g/mol
- Frações de baixa massa molar
- Disponibilidade de membranas

OSMOMETRO DE ZIMM

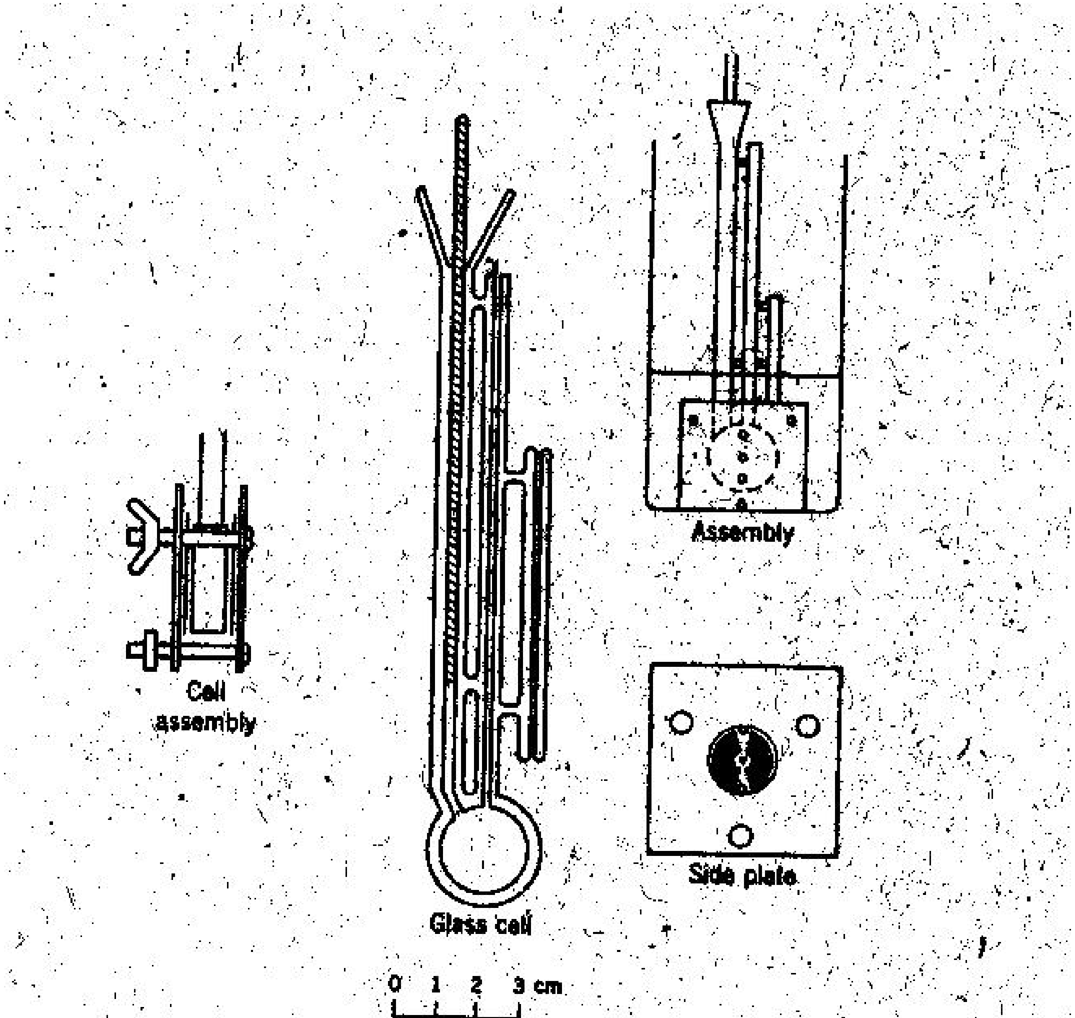
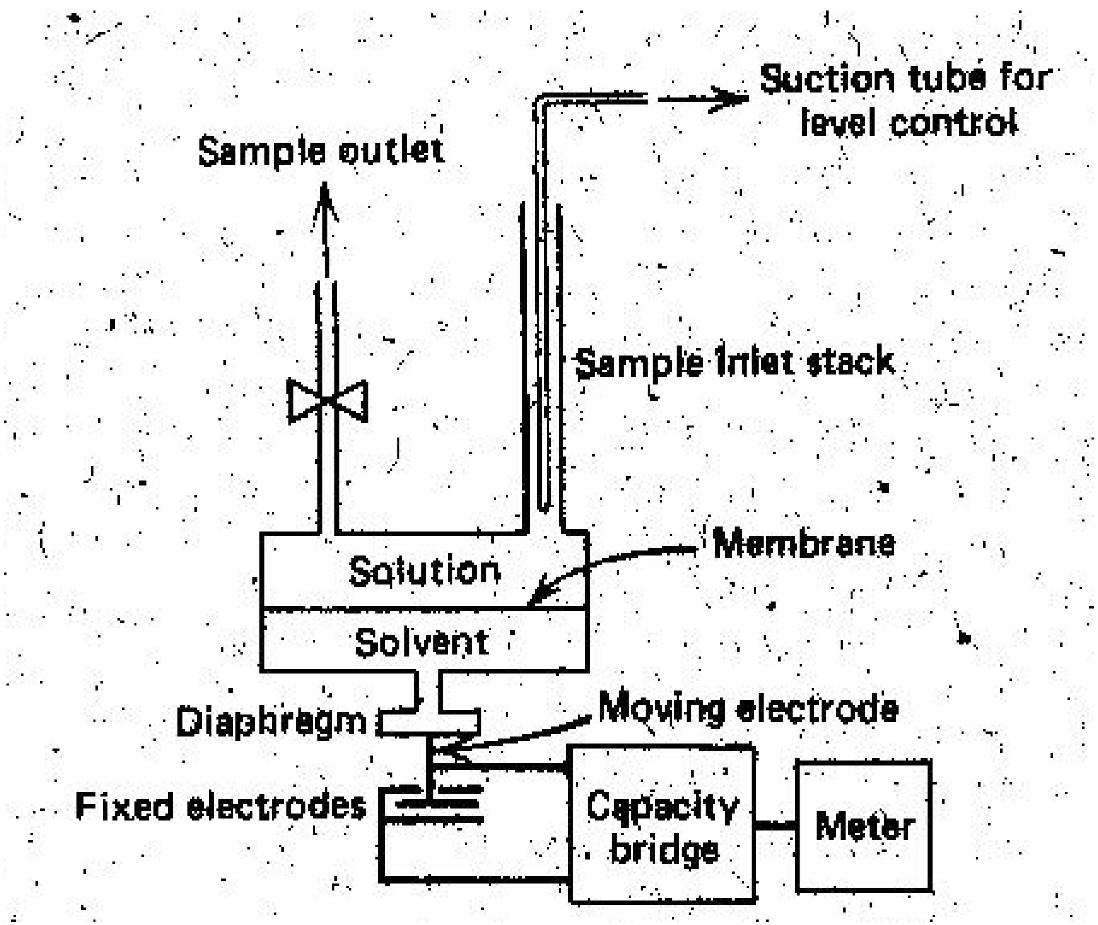


Diagram of the Zimm–Myerson osmometer (Zimm 1946). A typical diameter for the meas-


Suction tube for
level control
Sample outlet
Sample inlet stack
Membrane
Solution
Solvent
Moving electrode
Diaphragm
Fixed electrodes
Capacity
bridge
Meter

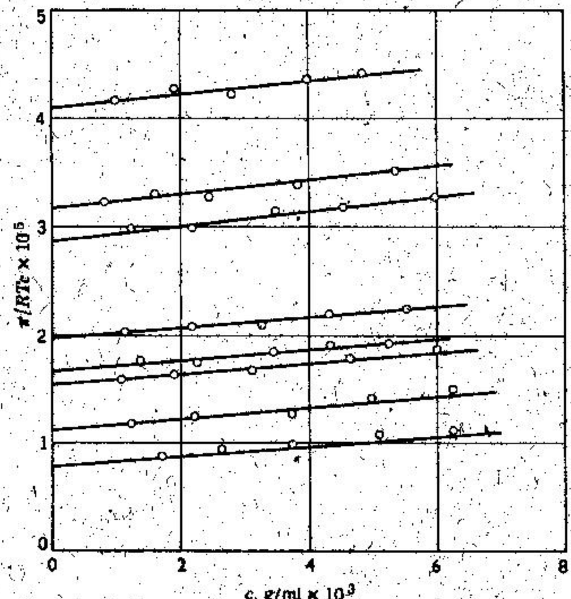


FIG. 8-5. Plots of $\pi/RTc = 1/\bar{M}_n$ versus c for cellulose acetate fractions in acetone solution (Badgley 1949).

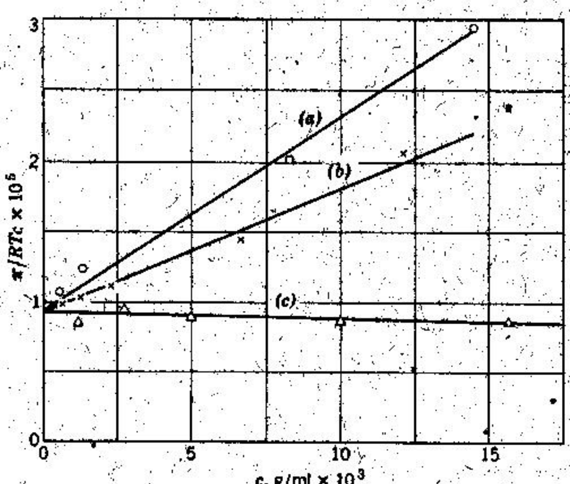


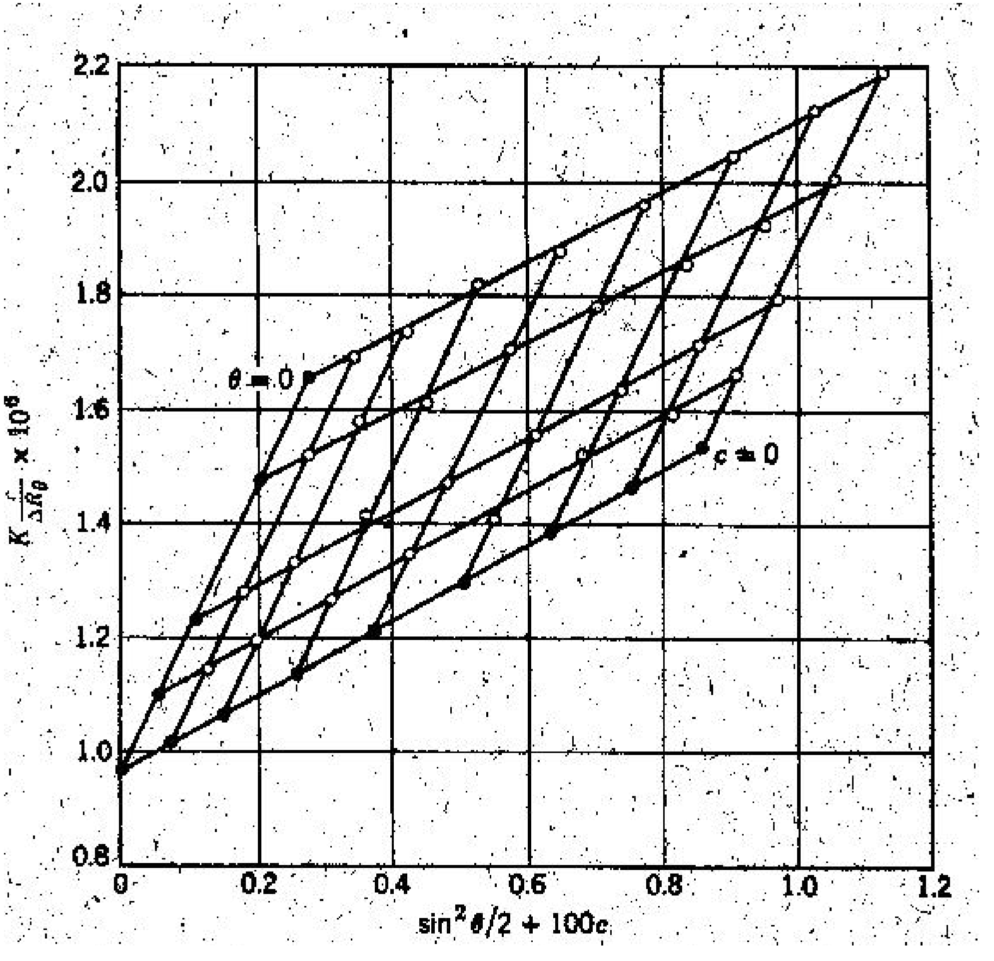
FIG. 8-6. Plot of $\pi/RTc = 1/\bar{M}_n$ versus c for nitrocellulose in (a) acetone, (b) methanol, and (c) nitrobenzene (Gee 1944, data of Dobry 1935).

$$\frac{\pi}{C_p} = \frac{RT}{\overline{M_n}} + A_2 C_p + A_3 C_p + \ldots\ldots$$

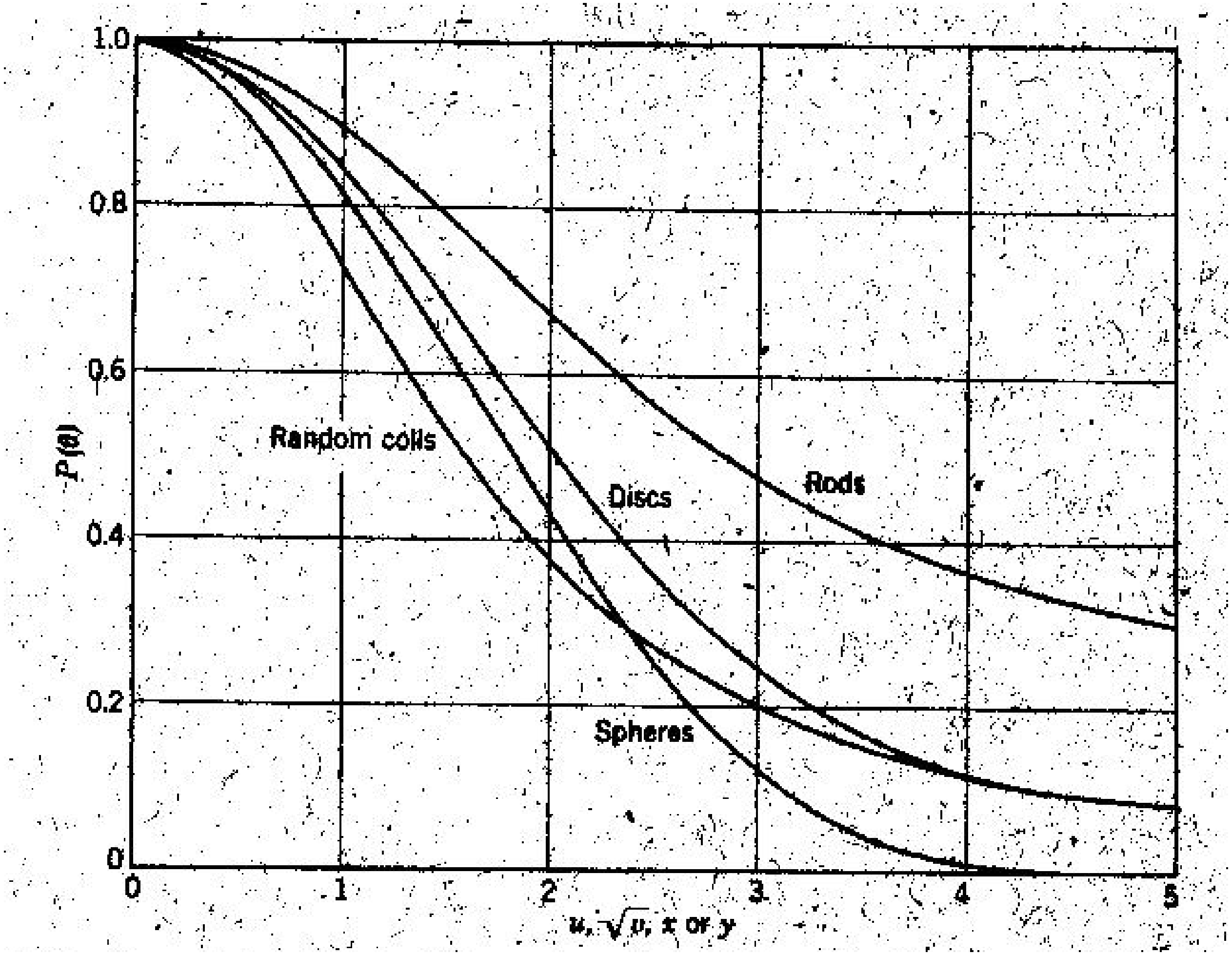
$$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i}$$

PLOT DE ZIMM

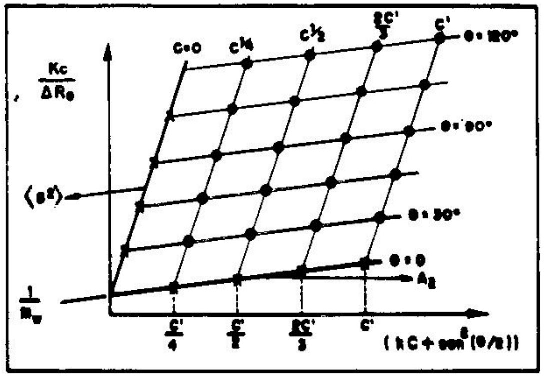
$$\frac{KC_p}{\Delta R_\theta} = \frac{1}{\overline{M_w}} + 2A_2C_p + 3A_3C_p^2 + ...$$



ESPALHAMENTO DE LUZ



PLOT DE ZIMM



$$\left[\frac{Kc}{\Delta R_\theta}\right]_{\theta \longrightarrow 0} = M_\omega^{-1} + 2A_2 \cdot c \qquad P^{-1}_{\theta \longrightarrow 0} \longrightarrow 1$$

$$\left[\frac{Kc}{\Delta R_\theta}\right]_{c \longrightarrow 0} = M_\omega^{-1} \cdot P^{-1}_{(q)}$$

$$P^{-1}_{(q)} = 1 + \frac{16\pi^2}{3\lambda_o^2} \langle S^2 \rangle_z \cdot \mathrm{sen}^2\, \theta/2 \qquad (1i)$$

$$\left(\frac{Kc}{\Delta R_\theta}\right)_{\theta \text{ e } c \longrightarrow 0} = \frac{1}{M_\omega}$$

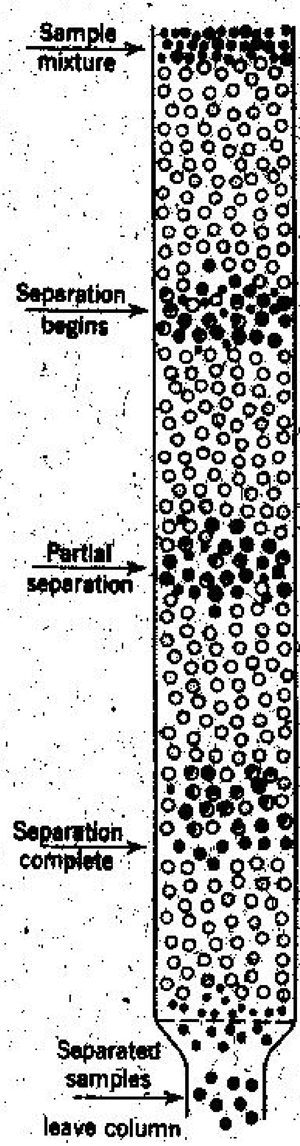
A inclinação para $\theta \longrightarrow 0$ $s = 2A_2$ (segundo coeficiente do virial)

A inclinação para $c \longrightarrow 0$

$$s = \frac{16\pi^2}{3\lambda_o^2} \langle S^2 \rangle_z M_\omega^{-1}$$

$$\overline{M_w} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

CROMATOGRAFIA DE EXCLUSÃO POR TAMANHO



$$\overline{M_w} = \frac{\sum n_i M_i^{\,2}}{\sum n_i M_i}$$

$$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i}$$

CALIBRAÇÃO UNIVERSAL

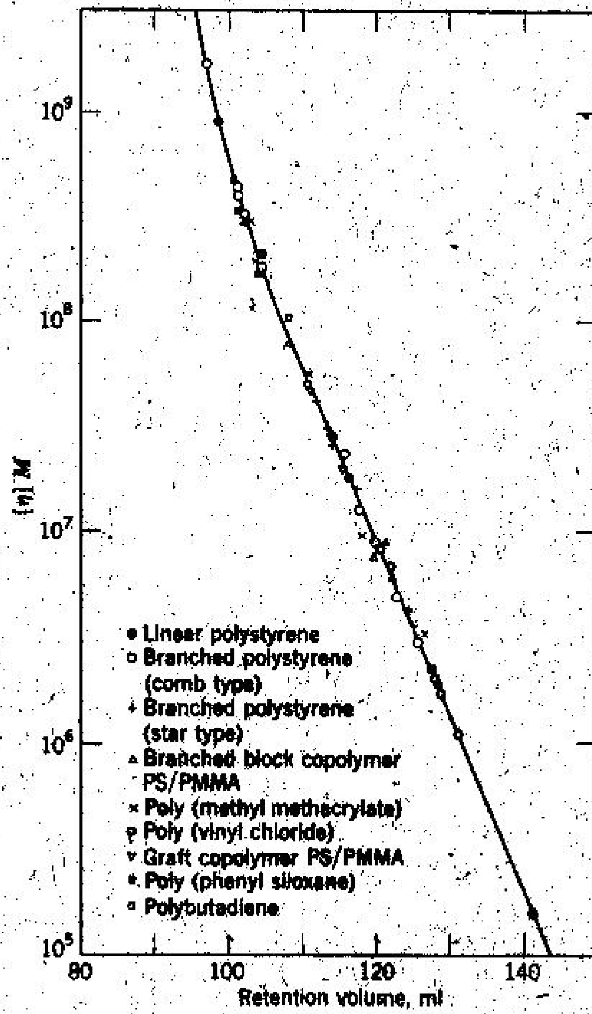


FIG. 8-15. Calibration curve for gel permeation chromatography based on hydrodynamic volume as expressed by the product $[\eta]M$ (Grubisic 1967). Among the polymer types shown are linear polystyrene, two types of branched polystyrene, poly(methyl methacrylate), poly(vinyl chloride), polybutadiene, poly(phenyl siloxane), and two types of copolymer.

DISTRIBUIÇÃO DE MASSA MOLECULAR

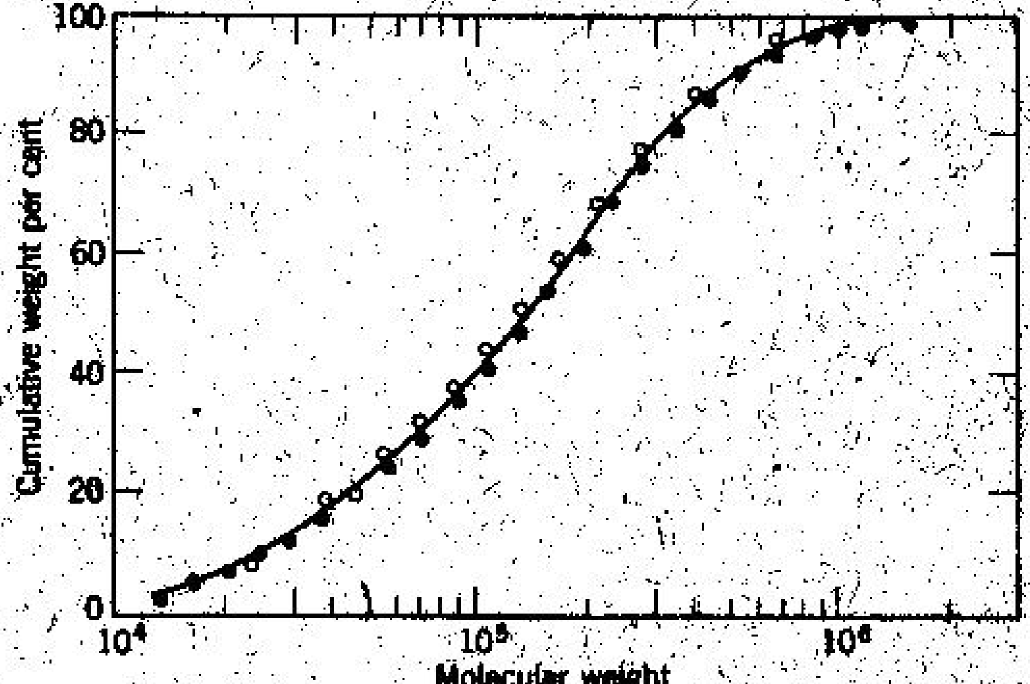


FIG. 8-16. Typical cumulative molecular-weight distribution curve for a sample of polypropylene (Crouzet 1969): gradient-elution data (○) and data from gel permeation chromatography (●). Molecular weight is plotted logarithmically because of the very broad distribution in this sample.

DISTRIBUIÇÃO DE MASSA MOLECULAR

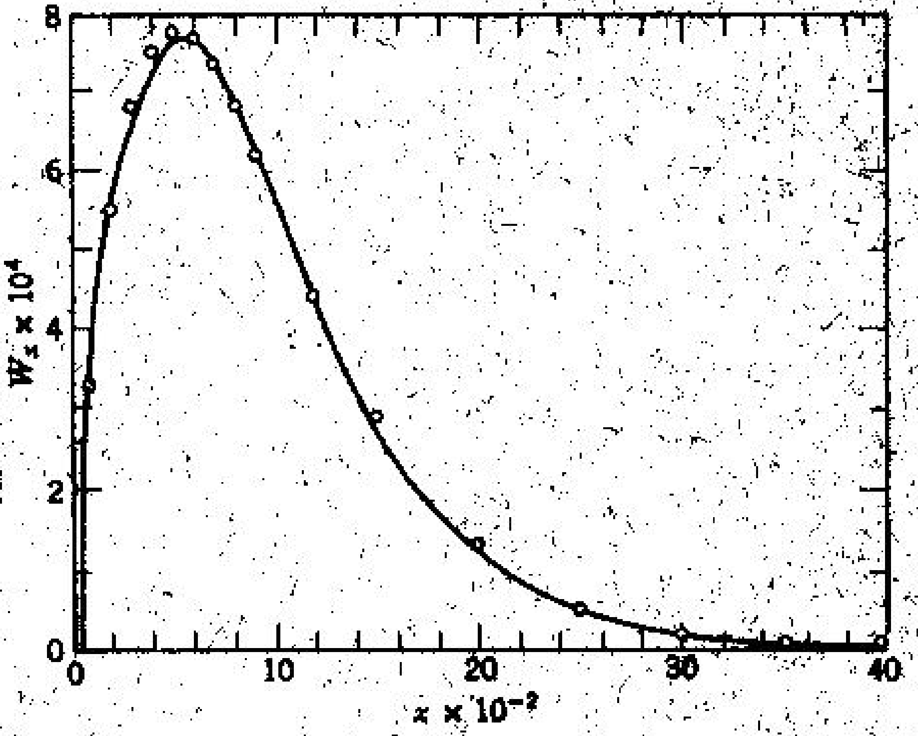


FIG. 8-17. Fit of gel permeation chromatography data for polystyrene to a molecular-weight distribution curve calculated from polymerization kinetics (May 1968).