

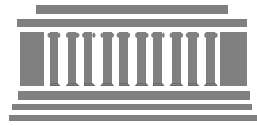
Crossover behavior in the dependence of the viscosity on concentration and molecular weight for semiflexible polymers

CONF-1901-220000

**V CHILEAN SYMPOSIUM
ON THE CHEMISTRY AND PHYSICAL CHEMISTRY OF POLYMERS**

G. C. Berry

Department of Chemistry



Carnegie Mellon University

Reprint manuscripts available on request
e-mail: gcberry@andrew.cmu.edu

Acknowledgments:

Partial Support:
National Science Foundation (GCB)

Concentration Ranges:

Several regimes of viscoelastic behavior are related to the mean separation Λ of molecular centers relative to the root-mean-square radius of gyration R_G :

$$\Lambda = (M/cN_A)^{1/3}$$

- **Infinite dilution** ($\Lambda \gg R_G$), describing the limiting behavior of $\tilde{\eta}$ as $c[\eta]$ tends to zero, such that $\tilde{\eta} - 1$ is equal to $c[\eta]$ (except possibly for charged chains under some conditions);
- **Dilute solutions** ($\Lambda > R_G$), defined loosely as the range of concentrations for which $(\eta_{sp} - 1)/c[\eta]$ begins to increase with increasing concentration, but is small enough that η_{sp} may be represented by a virial expansion in $c[\eta]$;
- **Moderately concentrated solutions** ($\Lambda < 2.5R_G$), for which the density of chains is large enough that certain thermodynamic and hydrodynamic interactions become progressively screened with increasing concentration, vitiating the use of a virial expansion to represent η_{sp} ; intermolecular entanglement effects may develop, depending on the molecular weight;
- **Concentrated solutions or bulk** ($\Lambda \ll R_G$), so that certain thermodynamic and hydrodynamic interactions are fully screened, and intermolecular entanglement effects may develop, depending on the molecular weight.

Dimensionless reduced viscosity $\tilde{\eta}$:

$$\tilde{\eta} = \eta / \eta_{\text{LOC}}^{(c)} = 1 + c[\eta]^{(c)}$$

- $[\eta]^{(c)}$ reduces to the intrinsic viscosity $[\eta]$ at infinite dilution. Expressions for $[\eta]^{(c)}$ will be considered for semiflexible chains in the following;
- $\eta_{\text{LOC}}^{(c)}$ is a "Local viscosity", tending to the solvent viscosity η_{solvent} at infinite dilution and to the "viscosity" η_{repeat} of a repeat unit for undiluted polymer. We will return to a discussion of $\eta_{\text{LOC}}^{(c)}$ in the following.

Molecular Parameters:

- L: contour length ($M_L = M/L$)
- R_G : radius of gyration (root-mean-square)
- R_H : hydrodynamic radius ($R_H = \Xi/6\pi\eta_{\text{solvent}}$)
- α : expansion factor
- γ_H : diameter to length ratio of hydrodynamic unit

$$[\eta] = [\eta]_{\text{FD}} K_\eta R_H / \gamma_H L$$

$$[\eta]_{\text{FD}} = \pi N_A R_G^2 \gamma_H / M_L$$

Thermodynamic Interactions:

For the wormlike model for a semiflexible chain:

$$R_G \approx \{ (\hat{a}L\alpha^2/3)^{-1} + (L^2/12)^{-1} \}^{-1/2}$$

$$\alpha \approx \left(1 + \hat{z} + k_\alpha (\hat{z}/2)^2 \right)^{-1/2}; \quad \nu \approx 3/5$$

$$\hat{z} = a_1 A(\hat{a}/L) z / (2\nu - 1)$$

$$z = (3d_T/16\hat{a})(3L/\pi\hat{a})^{1/2} \approx 0.18(d_T/\hat{a})(L/\hat{a})^{1/2}$$

Hydrodynamic Interaction:

$$K_\eta R_H \approx \{ [(10/3)(R_H)_{ND}]^{-2} + [(R_H)_{FD}]^{-2} \}^{-1/2}$$

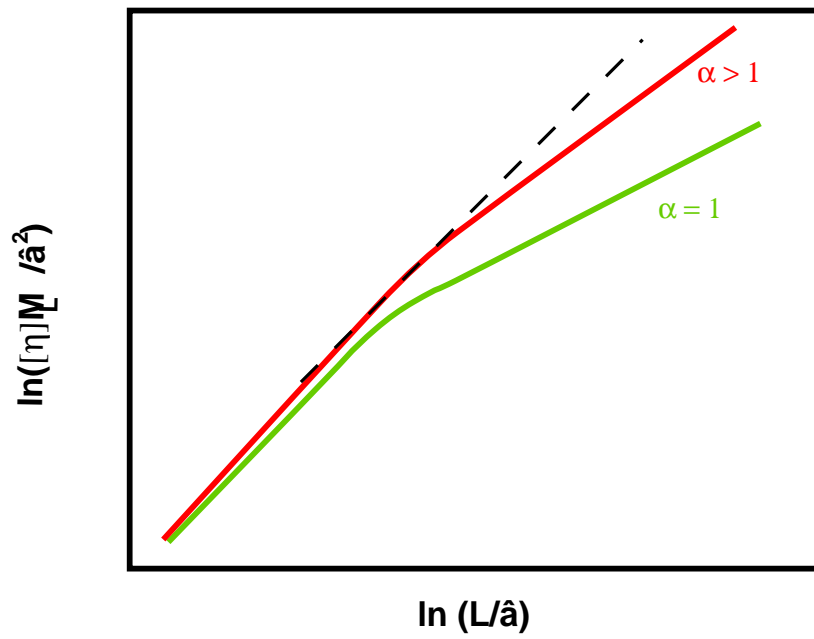
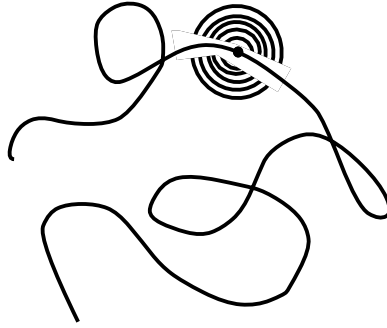
where

$$(R_H)_{ND}/L = \{ 2 \cdot 3^{1/2} / 9 \} (\hat{a}/L)^{1/2} \alpha; \quad (R_H)_{FD}/L = f(L/l, \gamma_H)$$

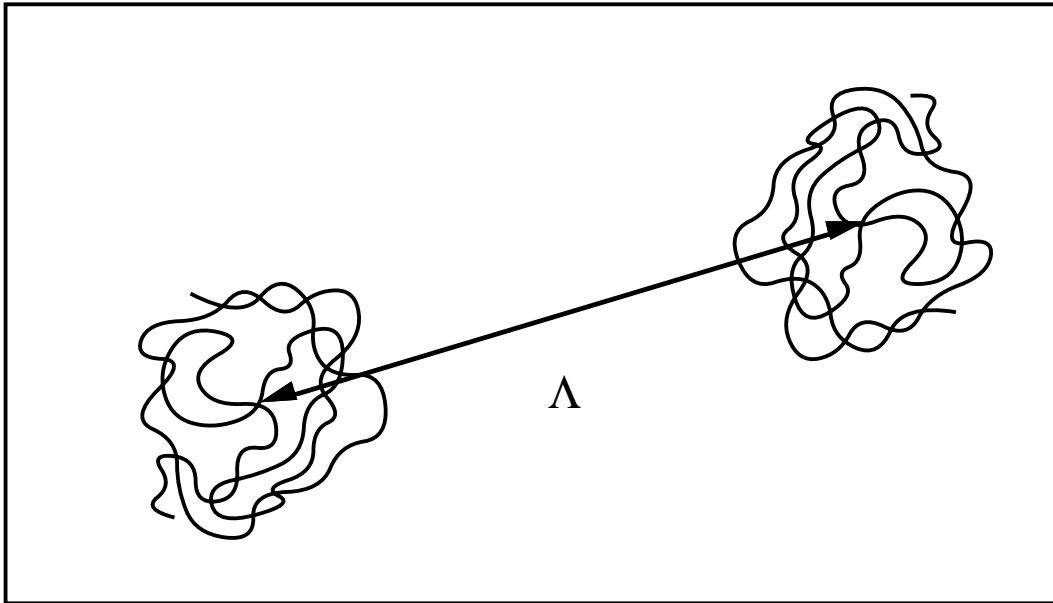
$$f(L/l, \gamma_H) \approx \zeta_{red} / \{ 1 + 2\kappa\zeta_{red} \ln(3L/2d_H) \}$$

$$\zeta_{red} = \gamma_H \zeta_l / 6\pi\eta_{LOC}^{(c)} d_H \propto \gamma_H$$

The Intrinsic Viscosity:



The Infinite Dilution Limit ($\Lambda/R_G \gg 1$):



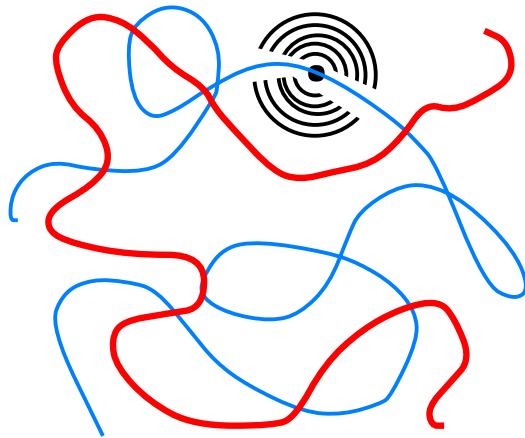
- $[\eta]^{(c)} \Rightarrow [\eta]$
- $\eta_{\text{LOC}}^{(c)} \approx \eta_{\text{solvent}}$

$$\tilde{\eta} = \eta/\eta_{\text{solvent}} = 1 + c[\eta]$$

With decreasing Λ/R_G (increasing c) the effects of screening of thermodynamic and hydrodynamic interactions become important, and are here expressed by the relation:

$$[\eta]^{(c)} = [\eta]_{FD}^{(c)} K_{\eta}^{(c)} R_H^{(c)} / \gamma_H L$$

$$[\eta]_{FD}^{(c)} = \pi N_A (R_G^{(c)})^2 \gamma_H / M_L$$



By analogy to the behavior at infinite dilution, $K_{\eta}^{(c)} R_H^{(c)}$ is represented by the expression:

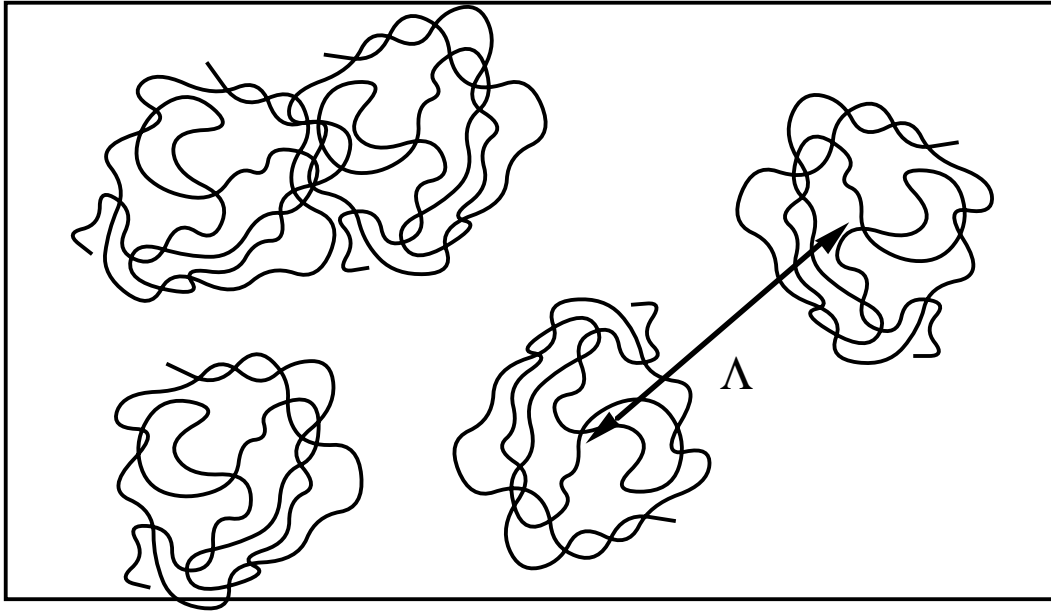
$$K_{\eta}^{(c)} R_H^{(c)} \approx \left\{ \left[(10/3) Q_{ND}(\Lambda/R_G) (R_H)_{ND} \alpha^{(c)}/\alpha \right]^{-2} + \left[Q_{FD}(\Lambda/R_G) (R_H)_{FD} \right]^{-2} \right\}^{-1/2}$$

where both $Q_{ND}(\Lambda/R_G)$ and $Q_{FD}(\Lambda/R_G)$ increase from unity with decreasing Λ/R_G (increasing c).

e.g., at infinite dilution:

$$K_{\eta} R_H \approx \left\{ \left[(10/3) (R_H)_{ND} \right]^{-2} + \left[(R_H)_{FD} \right]^{-2} \right\}^{-1/2}$$

Dilute Solutions:



- $\eta_{\text{LOC}}^{(c)} \approx \eta_{\text{solvent}}$
- $R_G^{(c)} \approx R_G$
- $K_\eta^{(c)} R_H^{(c)}$ increases with decreasing Λ/R_G (increasing c)

$$K_\eta^{(c)} R_H^{(c)} \approx \left\{ \left[\frac{10}{3} (R_H)_{\text{ND}} Q_{\text{ND}} (\Lambda/R_G) \right]^{-2} + \left[Q_{\text{FD}} (\Lambda/R_G) (R_H)_{\text{FD}} \right]^{-2} \right\}^{-1/2}$$

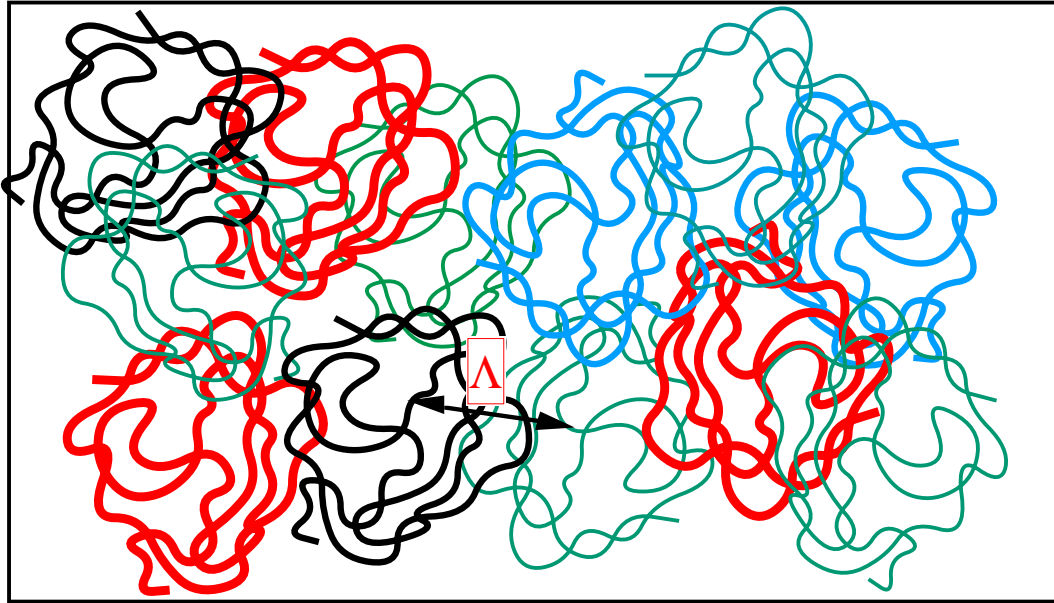
On expanding Q_{ND} and Q_{FD} in a Taylor series with respect to $c[\eta]$:

$$\begin{aligned} K_\eta^{(c)} R_H^{(c)} / K_\eta R_H &= 1 + k'c[\eta] + k''(c[\eta])^2 + \dots \\ &\approx \exp\{k'c[\eta]\} \approx (1 + c[\eta])^{k'} \end{aligned}$$

Thus, for dilute solutions:

$$\eta/\eta_{\text{solvent}} = 1 + c[\eta] + k'(c[\eta])^2 + k''(c[\eta])^3 + \dots$$

Moderately concentrated solutions:



- The distribution of molecular centers is *liquid-like*
- $\eta_{\text{LOC}}^{(c)} \approx \eta_{\text{solvent}}(1 + b\phi) \approx \eta_{\text{solvent}} \exp(b\phi)$ for small $b\phi$
- $R_G^{(c)}$ decreases toward R_G with decreasing Δ/R_G ($\alpha^{(c)}$ decreases toward unity)
- $K_\eta^{(c)} R_H^{(c)} / \gamma_H L$ increases toward unity with decreasing Δ/R_G
- $[\eta]^{(c)}$ increases from $[\eta]$ toward $[\eta]_{\text{FD}}^{(c)}$:

$$[\eta]_{\text{FD}}^{(c)} = \pi N_A (R_G^{(c)})^2 \gamma_H / M_L$$

(In the absence of chain entanglements)

$$\alpha^{(c)} \approx \text{MAX}\{1; \alpha(1 + [7(R_G/\Lambda)^3]^2)^{-1/16}\}$$

Rearranging the expression for $K_\eta^{(c)} R_H^{(c)}$:

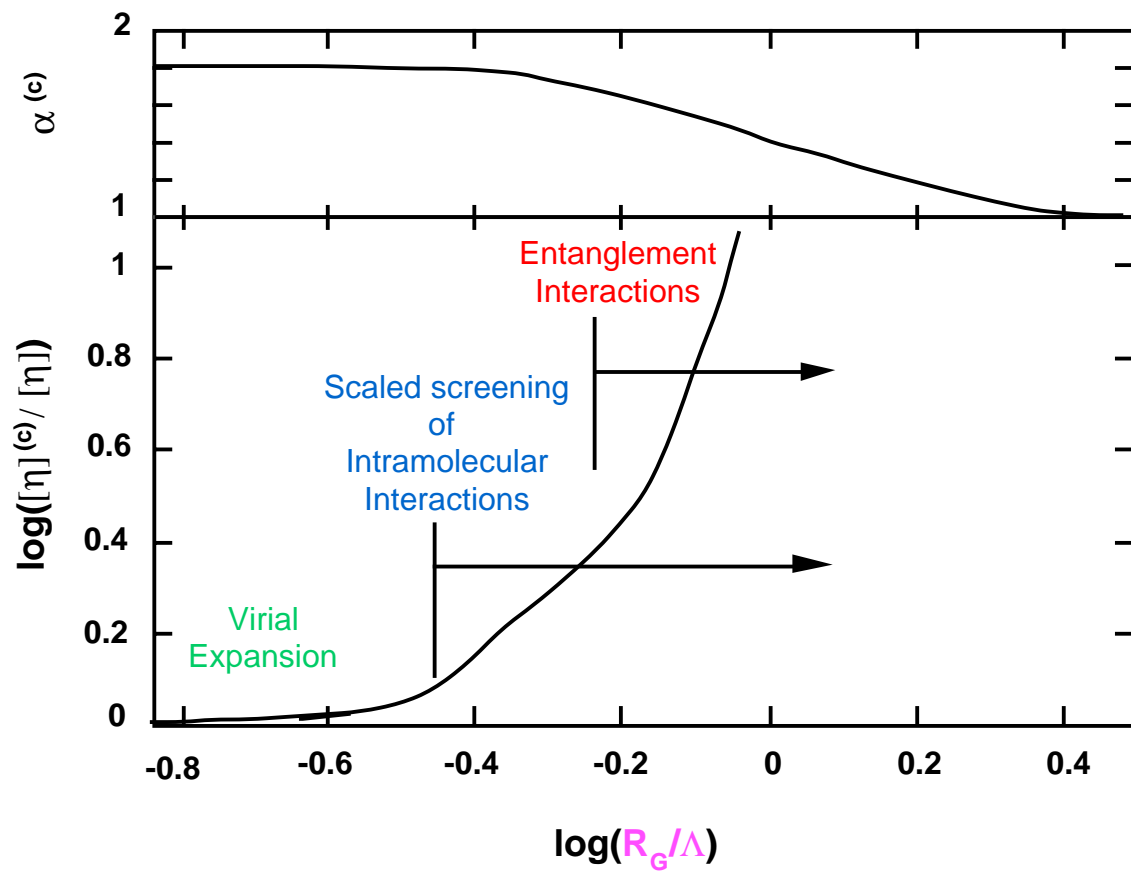
$$K_\eta^{(c)} R_H^{(c)} / L \approx \gamma_H Q_{FD} \{1 + (9Q_{FD}/20Q_{ND} \alpha^{(c)})^2 (3L/\hat{a})\}^{-1/2}$$

Empirically, for moderately concentrated solutions:

$$K_\eta^{(c)} R_H^{(c)} / L \approx \gamma_H (c/\rho)^\beta; \quad \gamma_H = d_H/l; \quad 0 \leq \beta \leq k'$$

Approximate relation (no chain entanglements):

$$[\eta]^{(c)} \approx \left[\{[\eta](1 + c[\eta])^{k'}\}^2 + \{\gamma_H (c/\rho)^\beta [\eta]_{FD}^{(c)}\}^2 \right]^{1/2}$$



Chain entanglements act to increase $K_{\eta}^{(c)}$ $R_H^{(c)}$:

$$[\eta]^{(c)} \approx \left[\{ [\eta](1 + c[\eta])^k \}^2 + \{ \gamma_H(c/\rho)^\beta [\eta]_{FD}^{(c)} \mathbb{E}(\tilde{X}/\tilde{X}_c) \}^2 \right]^{1/2}$$

$$\tilde{X} = c[\eta]_{FD}^{(c)}$$

$\tilde{X}_c = \text{constant} \approx 100$; empirical for many systems

$$\mathbb{E}(y) \approx \{1 + [y^2 m(y)]^2\}^{1/2}$$

$$m(y) \approx \{1 + \mu y^{-1/2}\}^3$$

$$m(\infty) = 1; \quad m(y) \approx y^{0.4} \text{ for } y < 100$$

$$\mathbb{E}(y) \approx \{1 + y^{4.8}\}^{1/2}$$

$$\eta = \eta_{LOC}^{(c)} \{1 + c[\eta]^{(c)}\}$$

Note:

The scaling of the screening of the thermodynamic and hydrodynamic interactions present in dilute solutions may each be scaled with the reduced variable

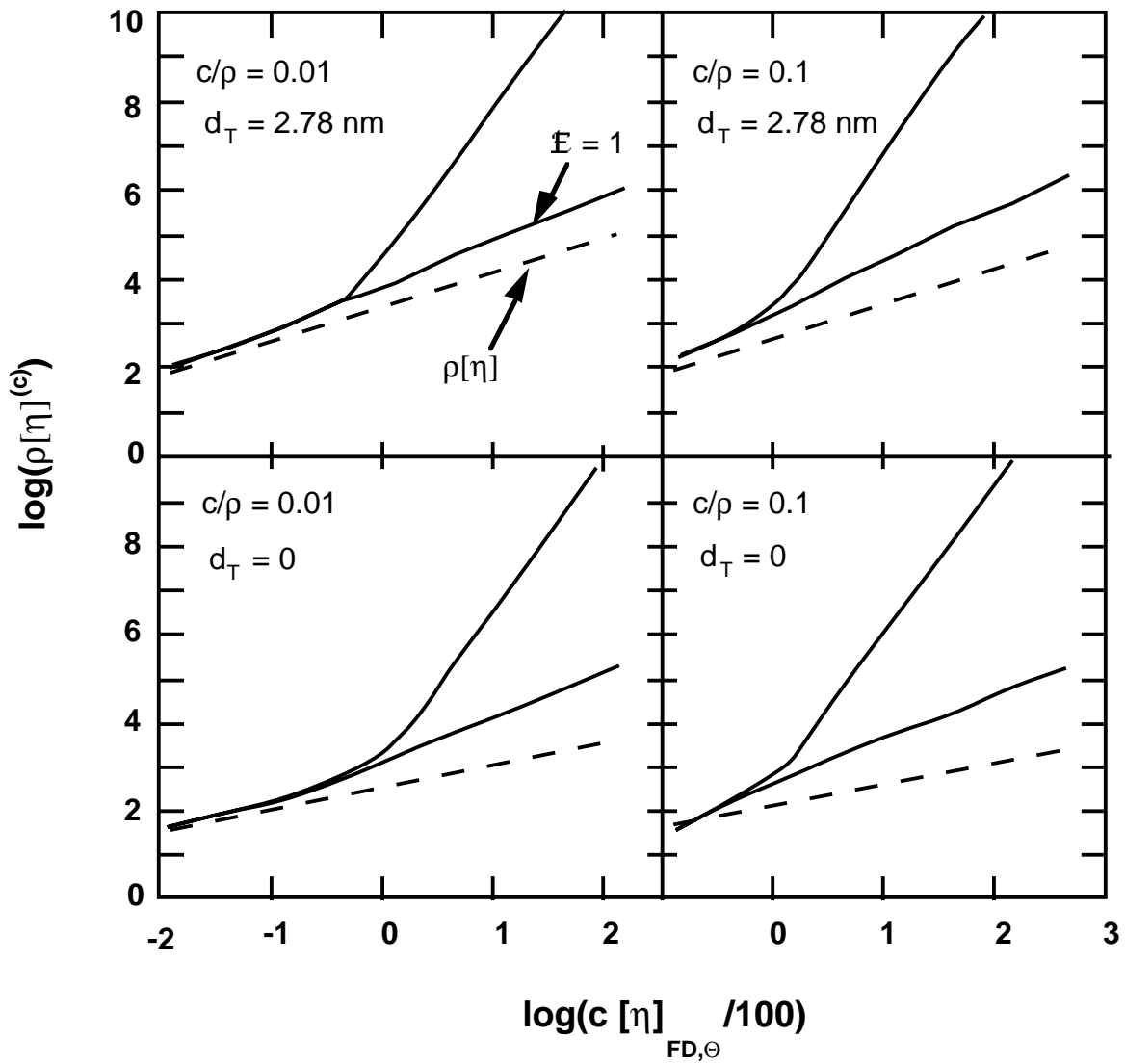
$$(R_G/\Lambda)^3 = cN_A R_G^3 / M = c/c^*$$

where $c^* = M/N_A R_G^3$.

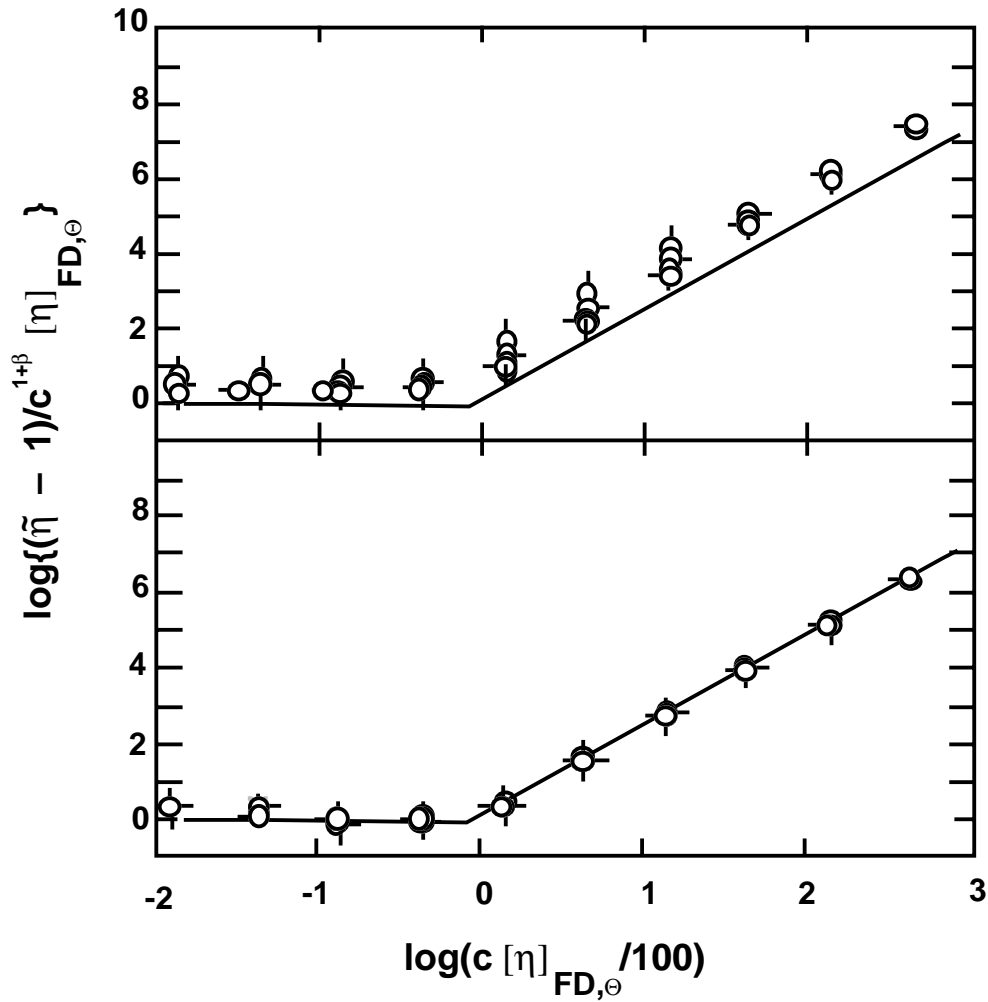
By contrast, the behavior following screening of these, and the development of entanglements scales with

$$\tilde{X} = c[\eta]_{FD}^{(c)} = \pi N_A (R_G^{(c)})^2 \gamma_H / M_L$$

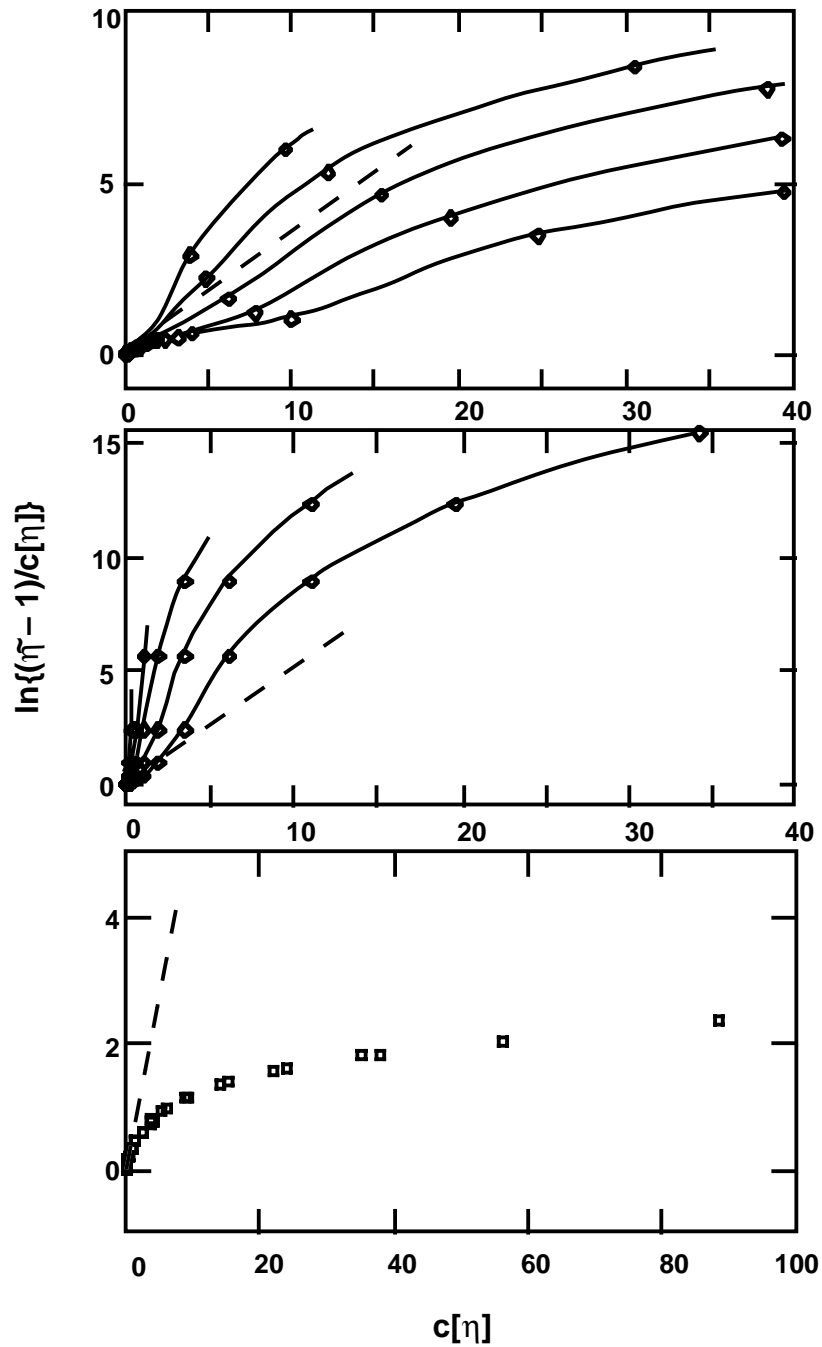
No single reduced concentration may be used to scale the reduced viscosity over the entire concentration range of interest.



- $\hat{a} = 1 \text{ nm}$ and $M_L = 400 \text{ nm}^{-1}$



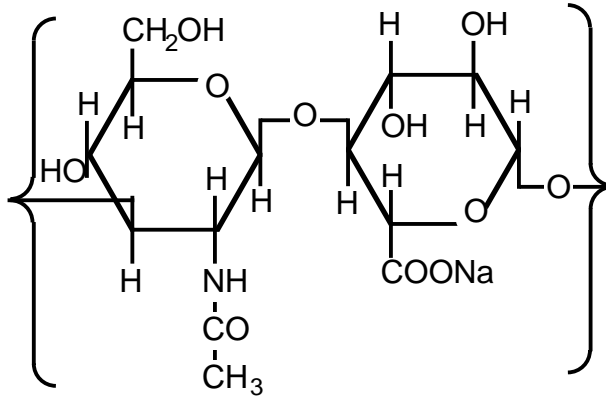
- $\hat{a} = 1 \text{ nm}$; $M_L = 400 \text{ nm}^{-1}$
- c/ρ is 0.01, 0.03, 0.1, 0.3 and 1
pip up, right, down, left and absent, respectively
- $\log(L/\text{nm})$ increasing from 2 to 5 in increments of 0.5
- d_T/nm equal to 0 (lower) and 2.78 (upper)



- c/ρ is 0.001, 0.003, 0.01, 0.03 and 0.01
 $\log(L/nm)$ increases from 2 to 5 in increments of 0.5
- $\hat{a} = 1 \text{ nm}; \quad M_L = 400 \text{ nm}^{-1}; \quad d_T = 2.78 \text{ nm}$
 $\hat{a} = 1 \text{ nm}; \quad M_L = 400 \text{ nm}^{-1}; \quad d_T = 0$
 $\hat{a} = 1000 \text{ nm}; \quad M_L = 400 \text{ nm}^{-1}; \quad d_T = 2.78 \text{ nm}$

Sodium hyaluronate

An acidic polysaccharide with a disaccharide repeat unit:



Recovered from animal connective tissue, synovial and vitreous fluids, and some bacteria.

For dilute solutions in 0.01 M NaCl,

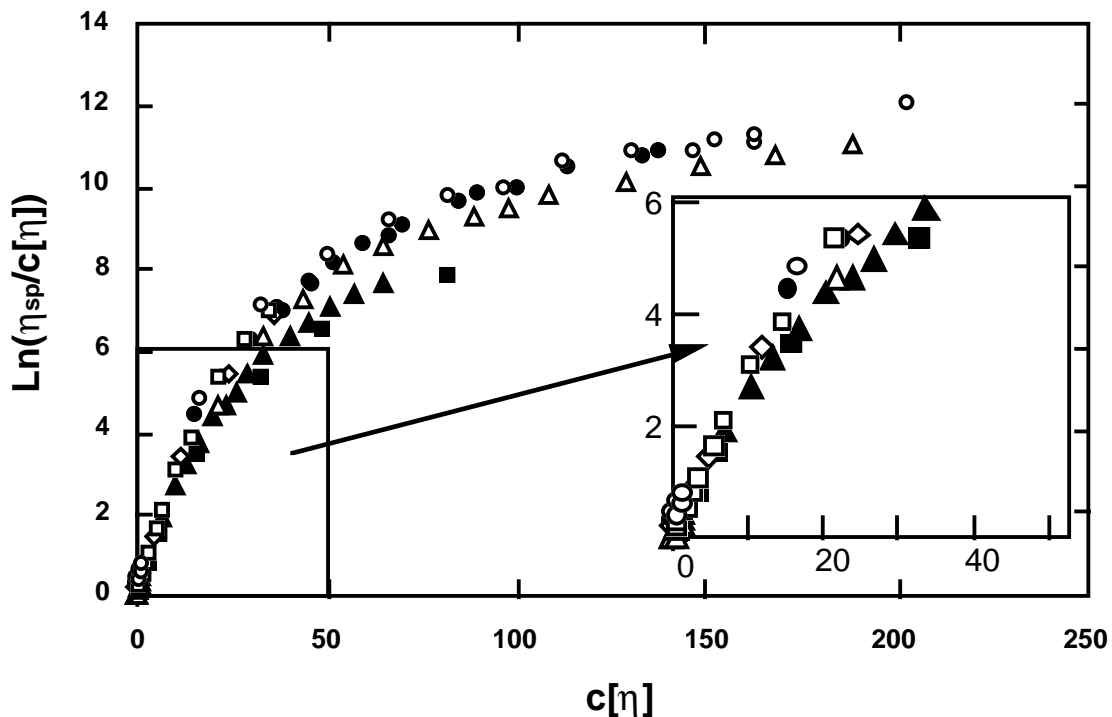
$$R_G/\text{nm} \approx 2.2 (\text{L}/\text{nm})^{0.5} \text{ from light scattering}$$

$$\text{For } L \gg \hat{a}: R_G^2 = \hat{a}L/3 \quad (\text{without excluded volume})$$

$$\therefore \hat{a} \approx 3 \times 2.2^2 = 14.5 \text{ nm}$$

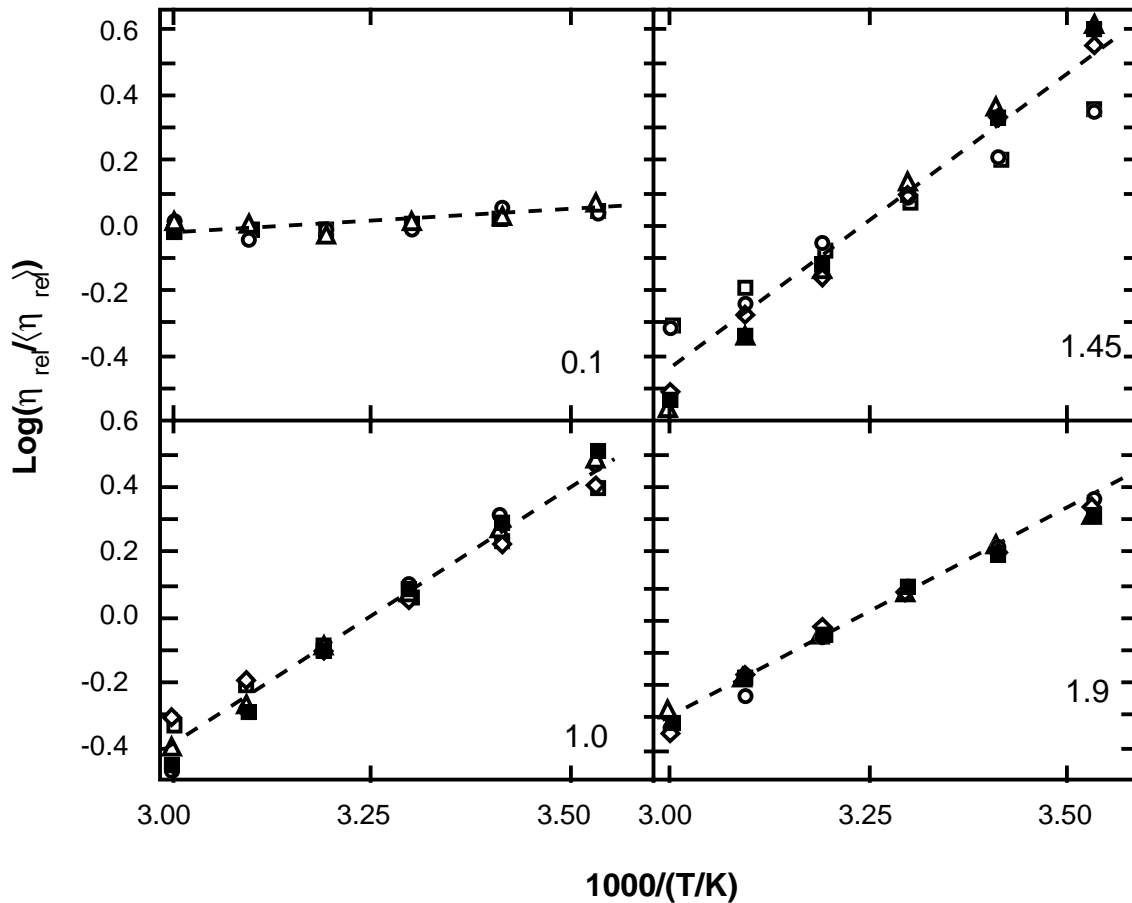
$$[\eta]/\text{mL} \cdot \text{g}^{-1} \approx 3.05 (\text{L}/\text{nm})^{0.82}$$

$$\partial \ln[\eta] / \partial \ln T \approx -1.8$$

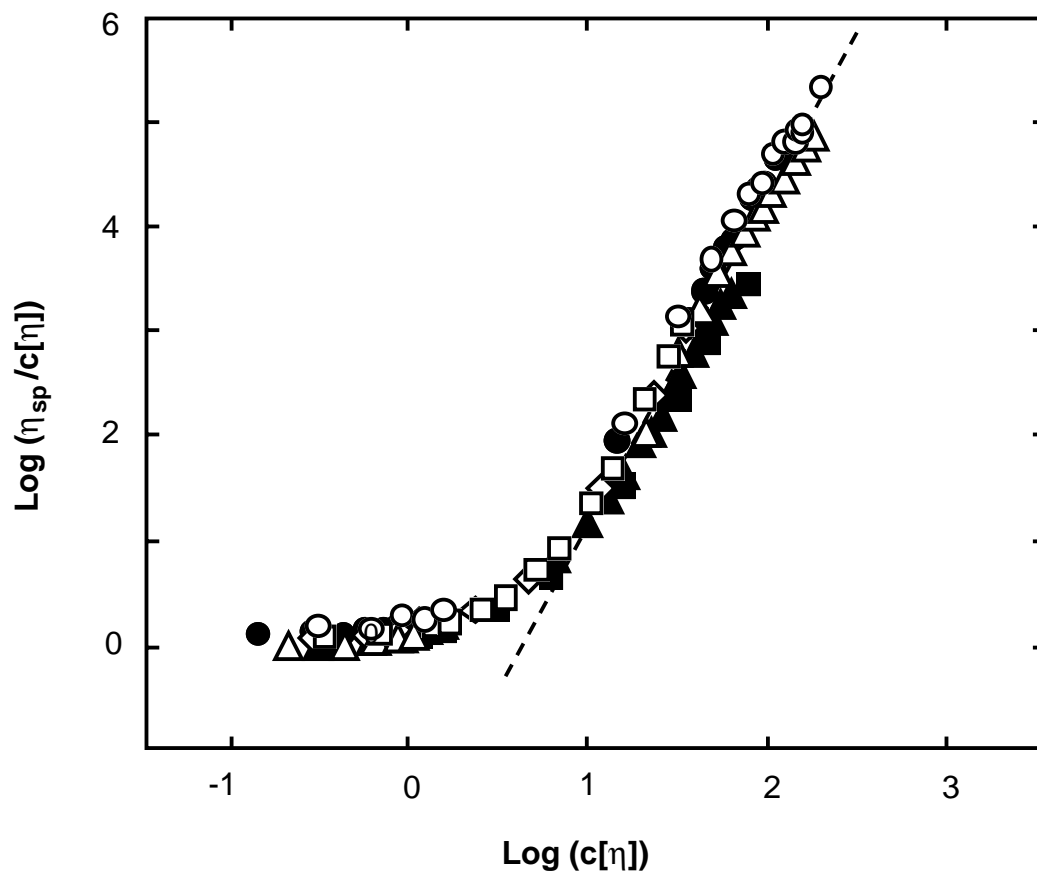


Sodium hyaluronate in aqueous 0.10 M NaCl at 25°C.

$10^{-6}M_w = 2.22, 2.00, 1.30, 1.00, 0.80, 0.35, \text{ and } 0.30$
(unfilled squares, circles, triangles and diamonds and the
filled circles, squares and triangles)

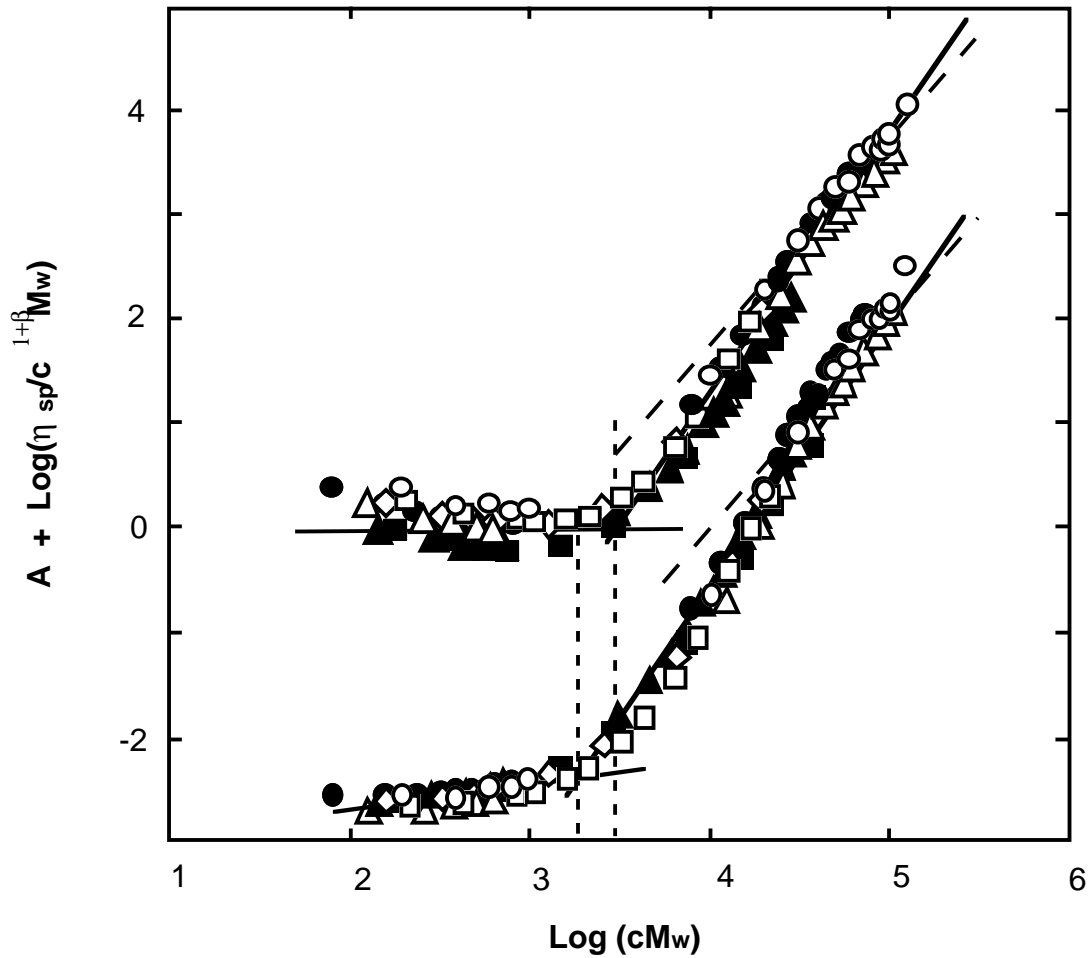


- $\langle \eta_{\text{rel}} \rangle$ is the avg. for the temperature interval (10 to 60°C)
- The nominal value of $\ln(c[\eta])$ is given for each panel.
- Very unusual behavior--normally $\partial \ln \eta_{\text{rel}} / \partial T^{-1}$ would increase monotonically with increasing c .

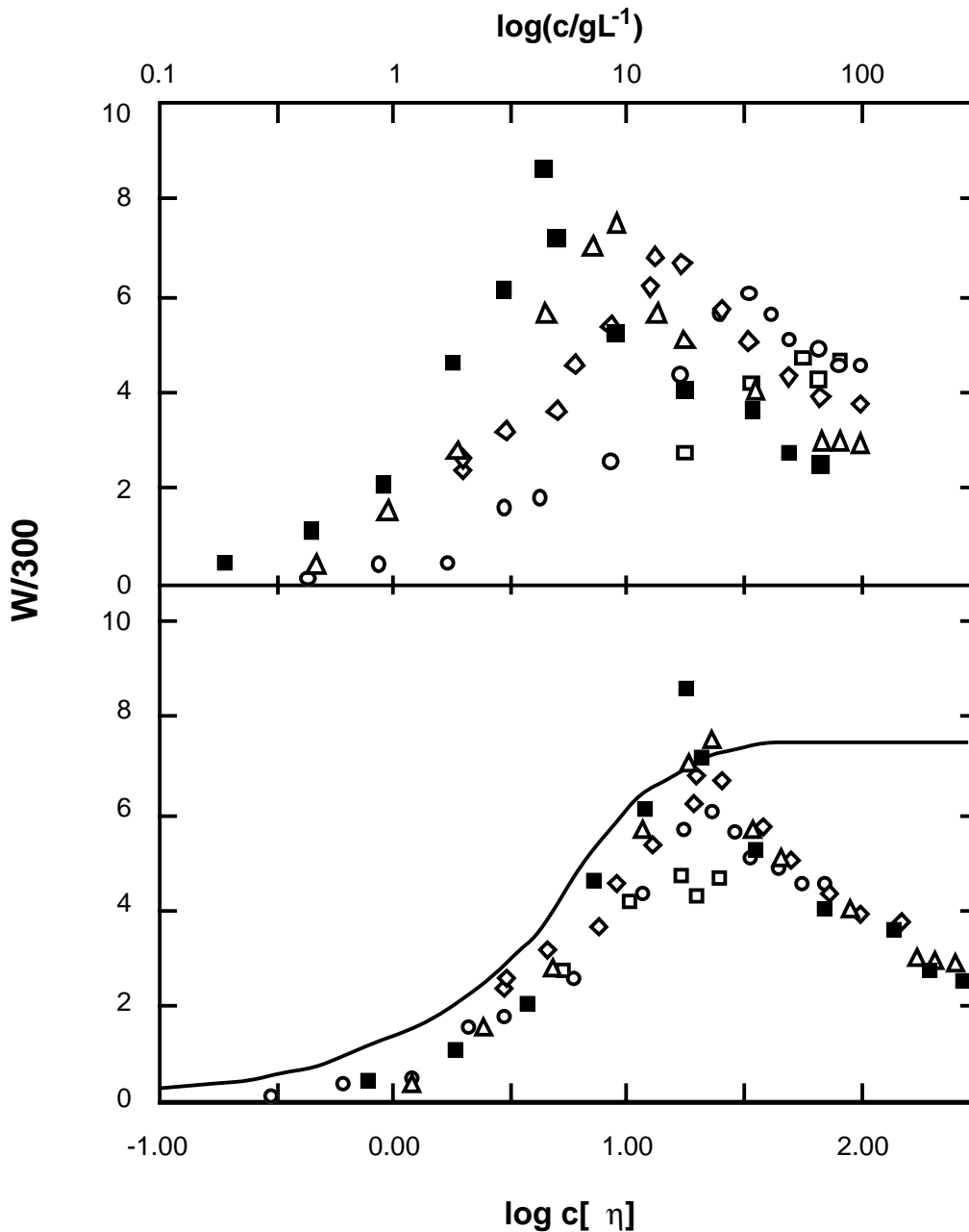


The dashed line has slope 3.15:

$$\eta/\eta_{\text{solvent}} \approx 1 + k_1 c[\eta] + c_2 (c[\eta])^{3.15}$$



- $\beta = 0$ (lower) or 0.5 (upper)
- solid lines and dashed lines for higher cM_w have slopes 2.4 and 2, resp.
- Transition gives $\hat{a}\gamma_H \approx 9-12$ nm; close to measured \hat{a}



- The slow increase is consistent with the known dependence of $[\eta]$ on T ($\partial \ln[\eta]/\partial \ln T \approx -1.8$); this reflects \hat{a} decreasing with increasing T
- The extremum is unexpected, and may reflect some decrease in the temperature dependence of \hat{a} through intermolecular effects; no theoretical treatment available.

More on the Local Viscosity:

Postulate: The dependence of $\eta_{\text{LOC}}^{(c)}$ on composition is similar to that of the viscosity η_{MIX} of mixtures of small molecules on composition.

In many treatments of η_{MIX} it is assumed that

$$\eta_{\text{MIX}} = A \exp[\Gamma(T, \{x\}, \dots)]$$

where $\{x\}$ is the set of mole fractions of the components.

With small molecule components at temperatures well above the T_g of any of the components, it is sometimes assumed that

$$\Gamma(T, \{x\}, \dots) \approx \sum_{\mu} x_{\mu} \Gamma_{\mu} + \sum_{\mu \neq \alpha} \Delta \Gamma_{\mu\alpha}$$

For example, then if all of the $\Delta \Gamma_{\mu\alpha} = 0$:

$$\ln(\eta_{\text{MIX}}) \approx \sum_{\mu} x_{\mu} \ln(\eta_{\mu})$$

Arrhenius (1887) utilized a similar expression with x_{μ} replaced by the volume fraction ϕ_{μ} of component μ .

In several treatments, $RT\Gamma_\mu$ is taken to be an **activation free energy for flow**, and is approximated as the **"ideal" free energy of mixing**, and the $RT\Delta\Gamma$ are the non-ideal "residual terms in the free energy of mixing. Thus for a binary mixture:

$$\ln(\eta_{\text{MIX}}) \approx (1-x_2)\ln(\eta_1) + x_2\ln(\eta_2) + \Delta\Gamma_{12}(x_2, T, \dots)$$

e.g., with $\Delta\Gamma_{12}(x_2) = x_2(1 - x_2)\gamma_{12}(T, \dots)$ a simple approximation, so that positive or negative curvature then results in plots of $\ln(\eta_{\text{MIX}})$ vs x_2 through the choice of γ_{12} .

A hybrid expression has been utilized for mixtures with at least one component with a T_g in the range of T of the experiment:

$$\Gamma(T, \{x\}, \dots) \approx \sum_{\mu} x_{\mu}\Gamma_{\mu} + \sum_{\mu \neq \alpha} \Delta\Gamma_{\mu\alpha} + \Psi(T - T_g, \dots)$$

In which case, for a binary mixture

$$\begin{aligned} \ln(\eta_{\text{MIX}}) \approx & (1-x_2)\{\ln(\eta_1) - \Psi_1(T - T_{g,1}, \dots)\} \\ & + x_2\{\ln(\eta_2) - \Psi_2(T - T_{g,2}, \dots)\} \\ & + \Delta\Gamma_{12}(x_2, T, \dots) + \Psi_{\text{MIX}}(T - T_g, \dots) \end{aligned}$$

With the Vogel relation for $\Psi(T - T_g, \dots)$:

$$\Psi(T - T_g, \dots) = \mathcal{K} / (T - T_g + \Delta)$$

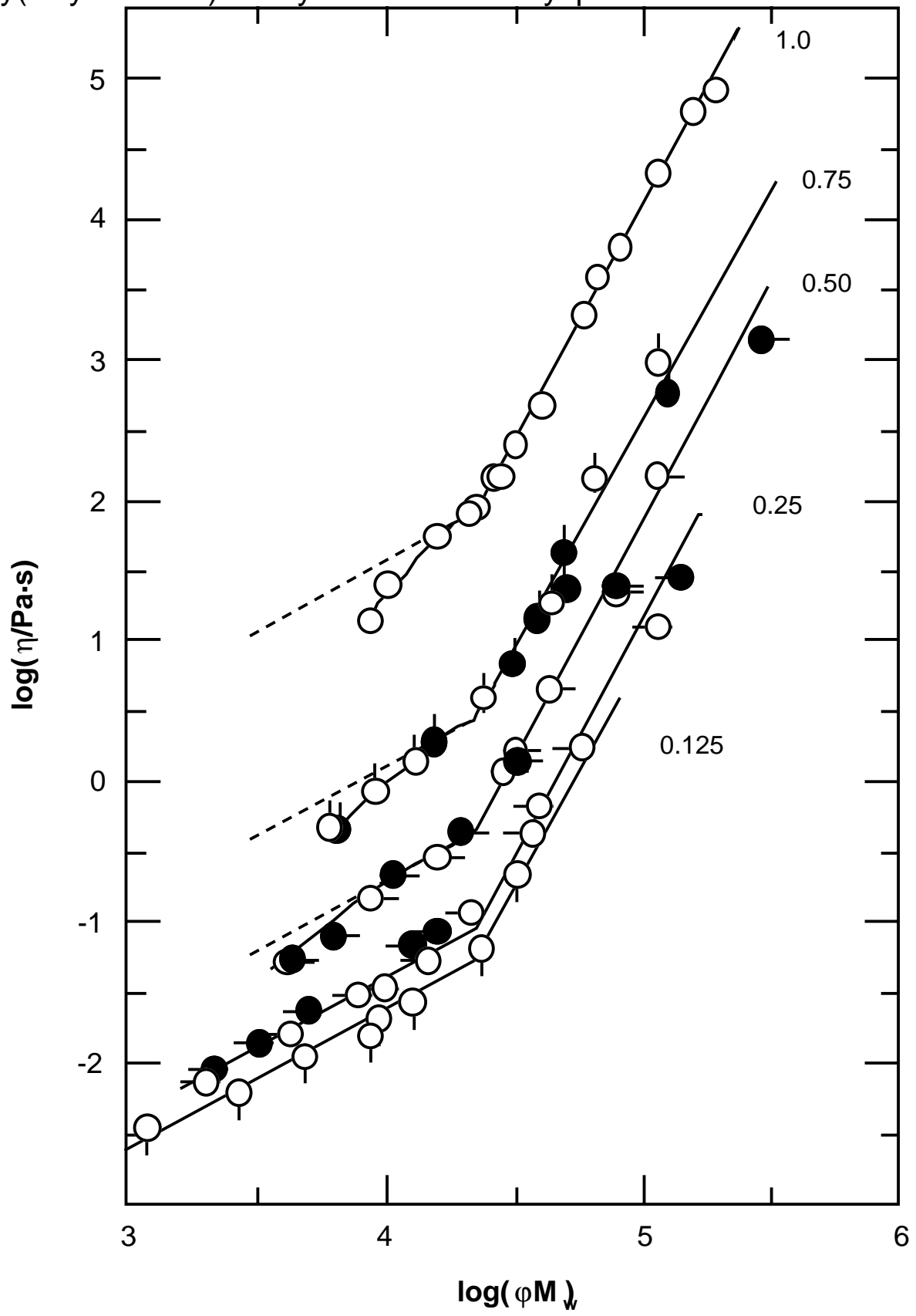
In the WLF approximation, \mathcal{K} and Δ are "universal" constants:
 $\mathcal{K} \approx 2300 \text{ K}$, $\Delta \approx 57.5 \text{ K}$.

There are very few data available to assess this expression for mixtures of small molecules.

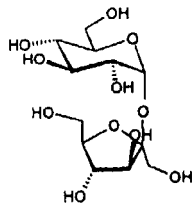
Three examples will be discussed:

- ◆ An example for poly(vinyl acetate) with η as a function of M at fixed ϕ , thereby fixed T_g (except for possible effects at low M) and fixed $\eta_{\text{Loc}}^{(c)}$
- ◆ An example for solutions of trehalose, a disaccharide with a relatively high T_g
- ◆ An example for polystyrene at a fixed M , as a function of T and ϕ

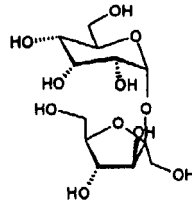
Poly(vinyl acetate): Cetyl alcohol & diethyl phthalate:



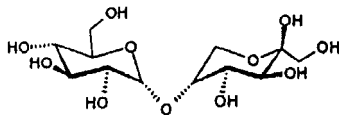
Aqueous solutions of Trehalose ($T_g \approx 120^\circ\text{C}$):



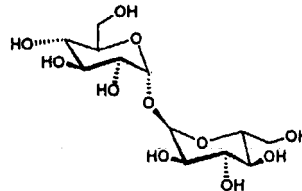
2-O- α -D-Glucopyranosyl- β -D-fructofuranoside (*Sucrose*)



2-O- α -D-allopyranosyl- β -D-Fructofuranoside (*Allosucrose*)



5-O- α -D-Glucopyranosyl- β -D-fructopyranose (*Leucrose*)



1-O- α -D-Glucopyranosyl α -D-glucopyranoside (*Trehalose*)

For this system,

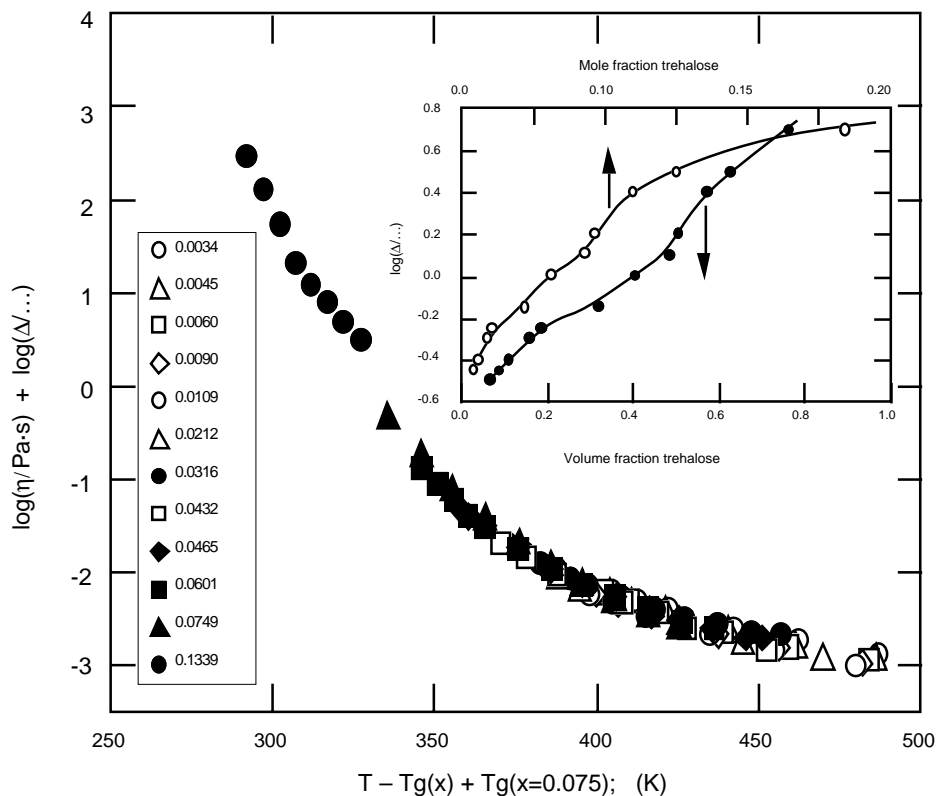
$$T_g = \frac{x_2 T_{g;2} + k(1 - x_2) T_{g;1}}{x_2 + k(1 - x_2)}$$

where k is a system-dependent (essentially empirical) constant, sometimes related to the difference in the volumetric thermal expansion of the two components.

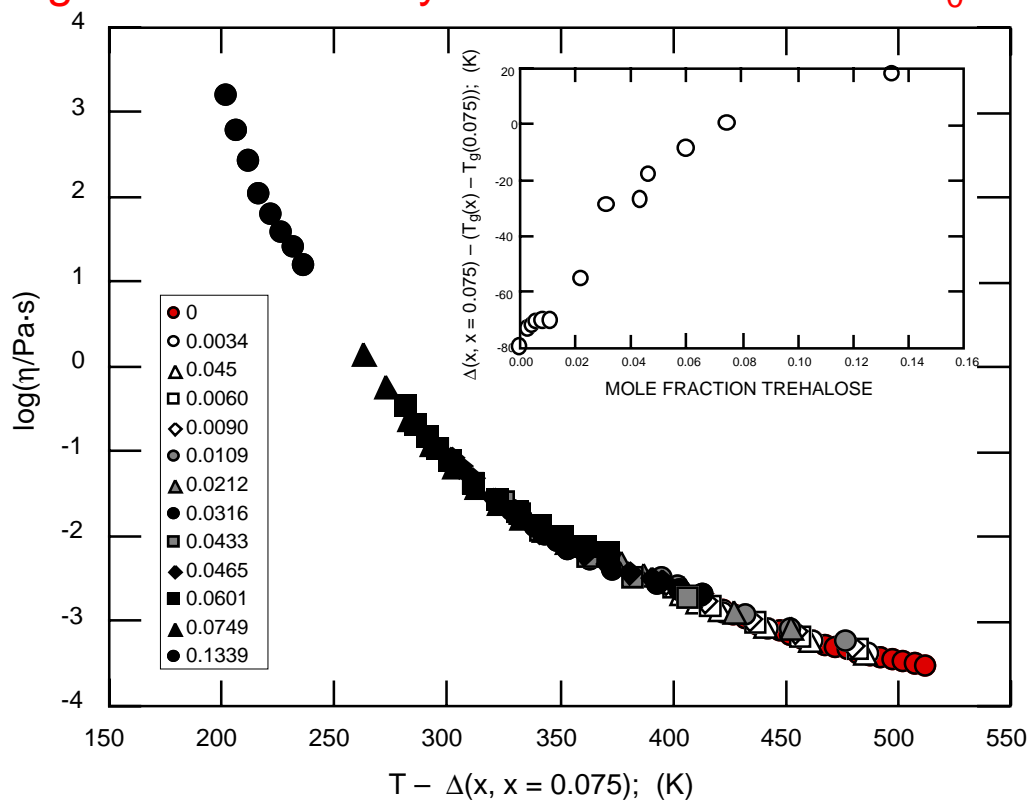
Two examples of possible correlations will be discussed:

- ◆ An example in which it is assumed that $\eta/K(x_2)$ should scale with $T - T_g(x_2)$, where $K(x_2)$ is some function of the mole fraction of trehalose, to be determined from the data.
- ◆ An example in which it is assumed that η should scale with $T - T_0(x_2)$, where $T_0(x_2)$ is a parameter to be determined from the data.

Assuming that a reduced viscosity should scale with $T - T_g$:



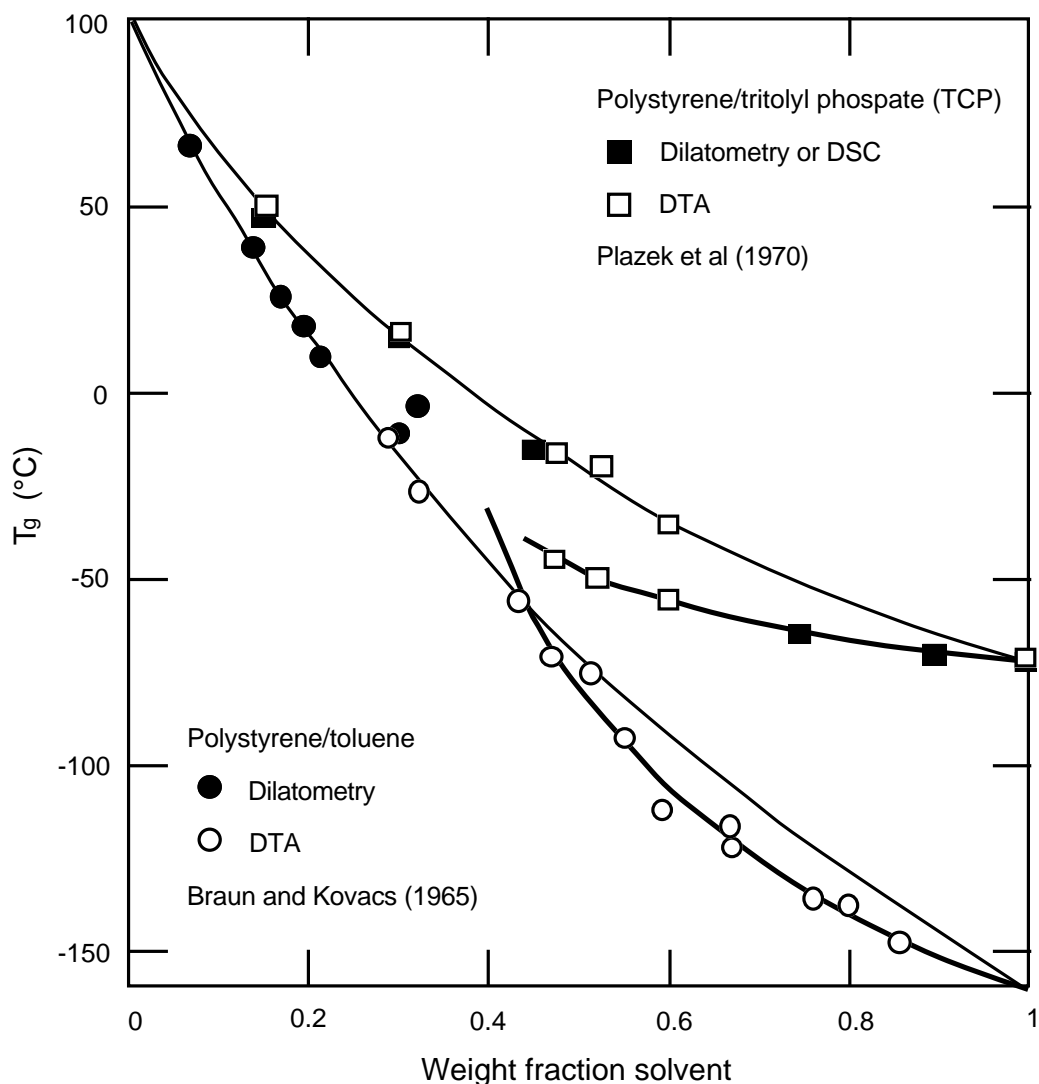
Assuming that the viscosity should scale with $T - T_0$:

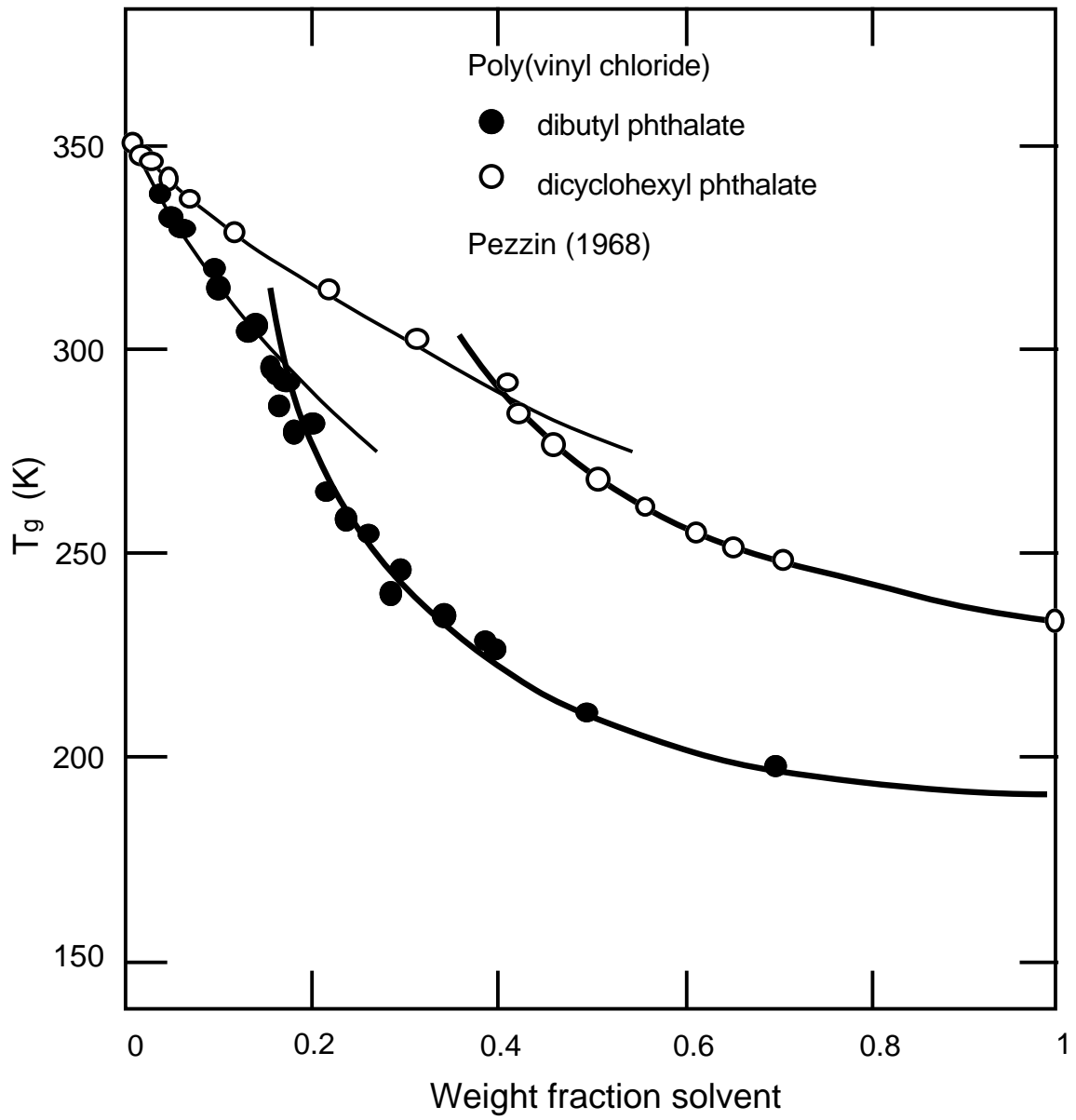


With some systems, it appears that two such expressions may be required to approximate T_g for the blend:

$$T_g = \text{Min} \left\{ \frac{x_2 T_{g;2} + k_1(1 - x_2) T_{g;02.}}{x_2 + k_1(1 - x_2)}, \frac{x_2 T_{g;\infty 1} + k_2(1 - x_2) T_{g;1}}{x_2 + k_2(1 - x_2)} \right\}$$

introducing additional empirical constants, and where $T_{g;2}$ for the polymer may depend approximately linear in $1/M_n$, and.





Polystyrene/styrene ($M_w = 2.4 \times 10^5$)

