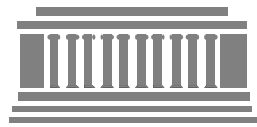


**Notes on Schroeder's minor scales:
Troubles with bare parameters in modeling macroscopic
properties**

Guy C. BERRY

Department of Chemistry

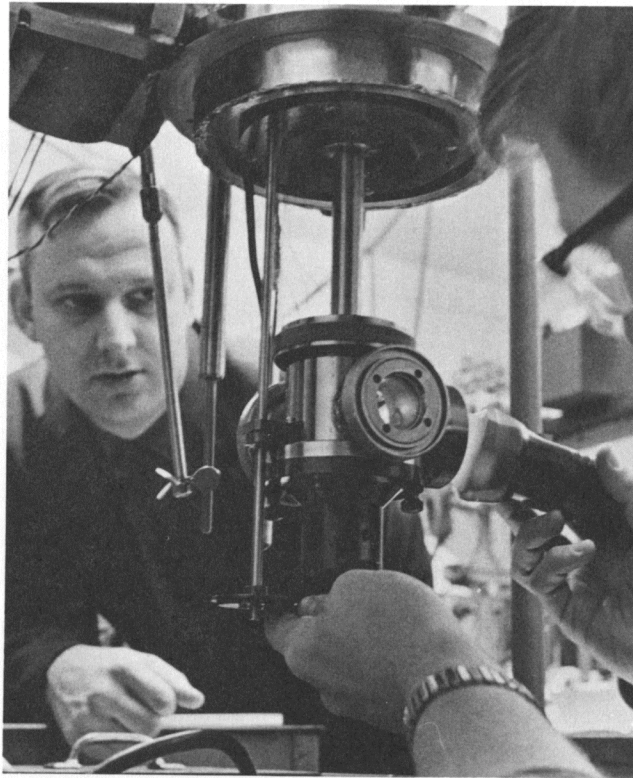


Carnegie Mellon University
Pittsburgh, PA, USA

"One upon a time, in the very, very distant and dark past, on the quest to become the perfect creep,..."

OR

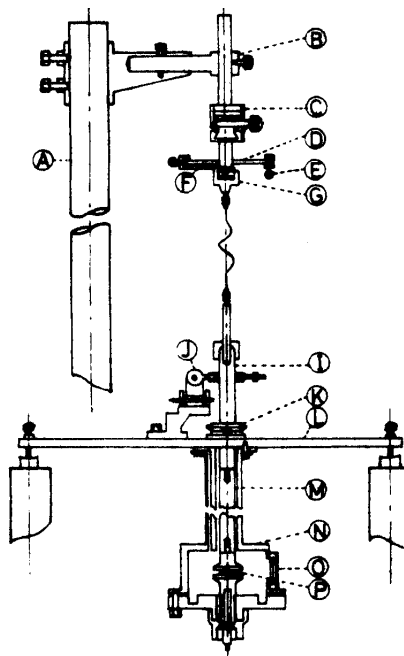
"Who is that "handsome" stranger?; Mister, will you put down your toys and come hold my football while I kickoff?--I don't trust Lucy!"



Inspecting specimen chamber of the magnetic suspension creep apparatus (D. J. Plazek, V. M. O'Rourke).

Said "J.D." to his new and eager young graduate student: "Donald, here is a drawing from the literature for an instrument called a "Torsion Pendulum". Please go build one for us, and do some experiments using the new apparatus".

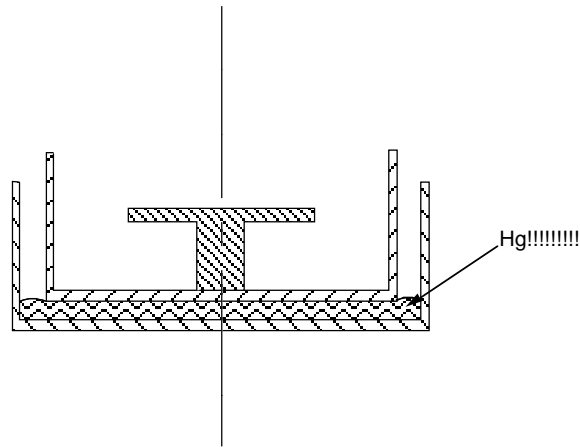
By the way, the drawing had no scale, and therein hangs a tail --oops, I mean tale; no reflection on DJP's "Devilish" personality!



Drawing from the Ph.D. Dissertation of Norio Nemoto, Institute for Chemical Research, Kyoto University, 1970 (My, he's getting to be of a "mature" age too, isn't he!)

Not all of DJP's ideas had an equal opportunity,

Or, how the lab was saved from mercury poisoning in the days before OSHA!



Fortunately for all, DJP found that as a personality, Hg was a scum, more prone to be a jerk than to faithfully creep along!

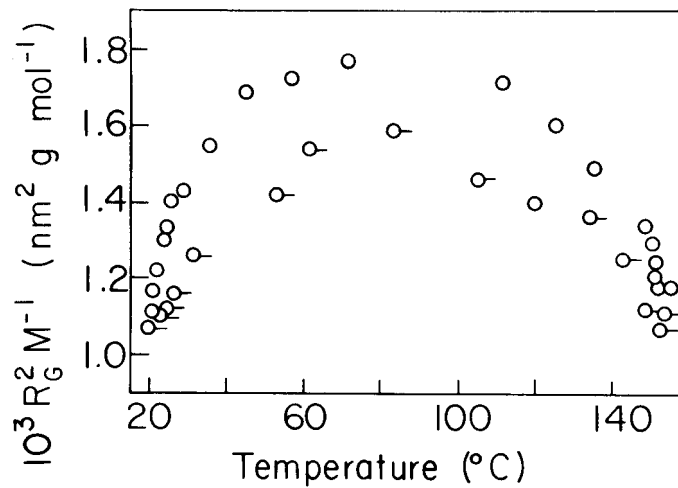
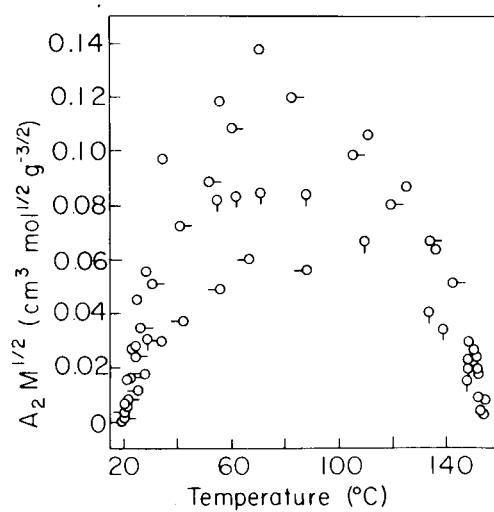
*It is wise to remember that
"Those who have never made a mistake
Are also those who have no accomplishments!"*

$$A_2 = A_2^{(\text{Rod})} A(z, L/\hat{a}, \tilde{h}); \quad A_2^{(\text{Rod})} = (\pi N_A / 4 M_L^2) d_T$$

$$R_G = R_G^{(0)} R(z, L/\hat{a}, \tilde{h})$$

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

Examples for Polystyrene in cyclopentane:



Despite its central role in predicting, say, $R_G/R_G^{(0)}$, the present ability to predict d_T is not much better than it was in 1960 when Walter Stockmayer opined that owing to the coarse-grained nature of the statistical mechanical calculations of R_G and A_2 ,

"Special and analytically convenient forms for (the pair potential of the average force, and hence d_T) $w(r)$... have no great fundamental significance, but almost any such function can be used with impunity, provided its short-range nature is preserved, as required by the inequality

$$\beta = 2\pi\hat{a}^2 d_T \ll R_G^3 \quad \dots"$$

(*Makromol. Chemie* (1960) 35: 54-74)

Here,

$$\beta = 4\pi \int_0^{\infty} dr \, r^2 \{1 - \exp(-w(r)/kT)\}$$

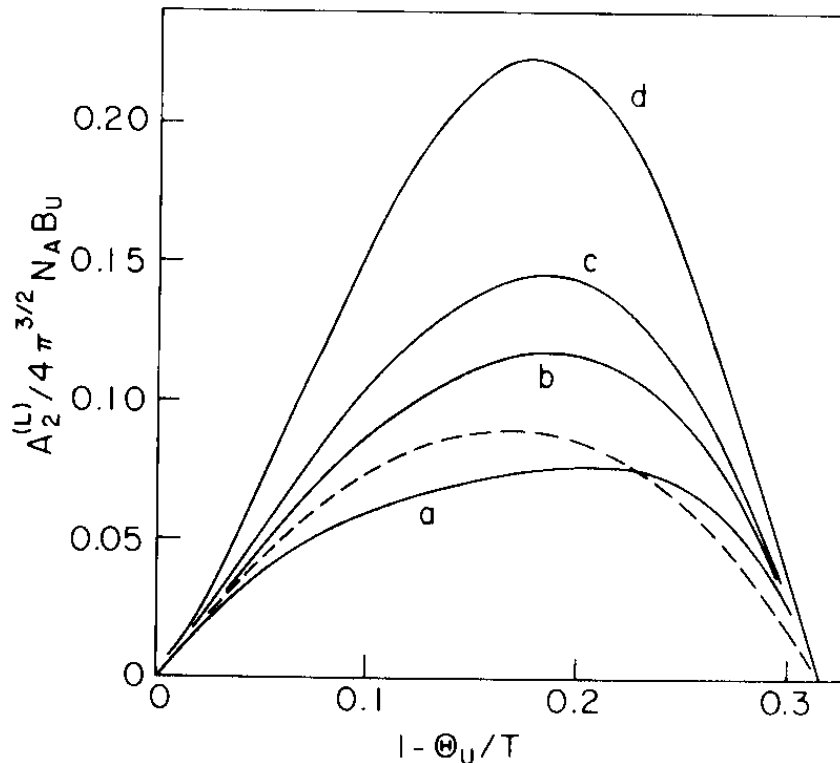
- In general, d_T must vanish when $A_2 = 0$, as at the upper or lower Flory theta temperatures, Θ_U and Θ_L , resp.
- For uncharged polymers, in the range $\Theta_U \leq T \leq \Theta_L$:

$$0 \leq d_T \leq d_{\text{Geometric}}$$

- Larger values of d_T may be obtained with charged polymers.
- In general, thermodynamic considerations require that for T near to Θ_U or Θ_L :

$$d_T = B_{U/L}(1 - \Theta_{U/L}/T) + \dots$$

- Example for Polystyrene in cyclopentane:



$$\eta = \eta_{\text{LOC}}^{(c)} H(\varphi, L/\hat{a}, d_H/\hat{a}, d_T/\hat{a})$$

The "local viscosity" $\eta_{\text{LOC}}^{(c)}$ is proportional to a "local friction factor" $\zeta_{\text{LOC}}^{(c)}$ divided by the scale ξ over which the friction occurs.

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

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, 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

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

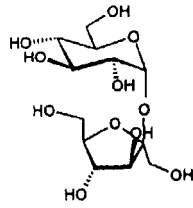
With the Vogel relation for $\Psi(T - T_g, \dots)$:

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

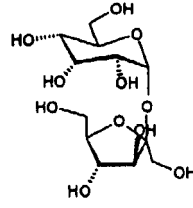
In the WLF approximation, \mathcal{K} and Δ are "universal" constants: $\mathcal{K} \approx 2300 \text{ K}$, $\Delta \approx 57.5 \text{ K}$.

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

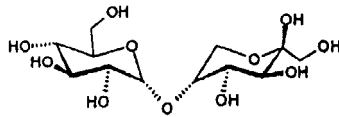
Aqueous solutions of Trehalose ($T_g \approx 120^\circ\text{C}$):



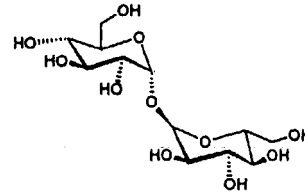
2-O- α -D-Glucopyranosyl- β -D-fructofuranoside (*Sucrose*)



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,

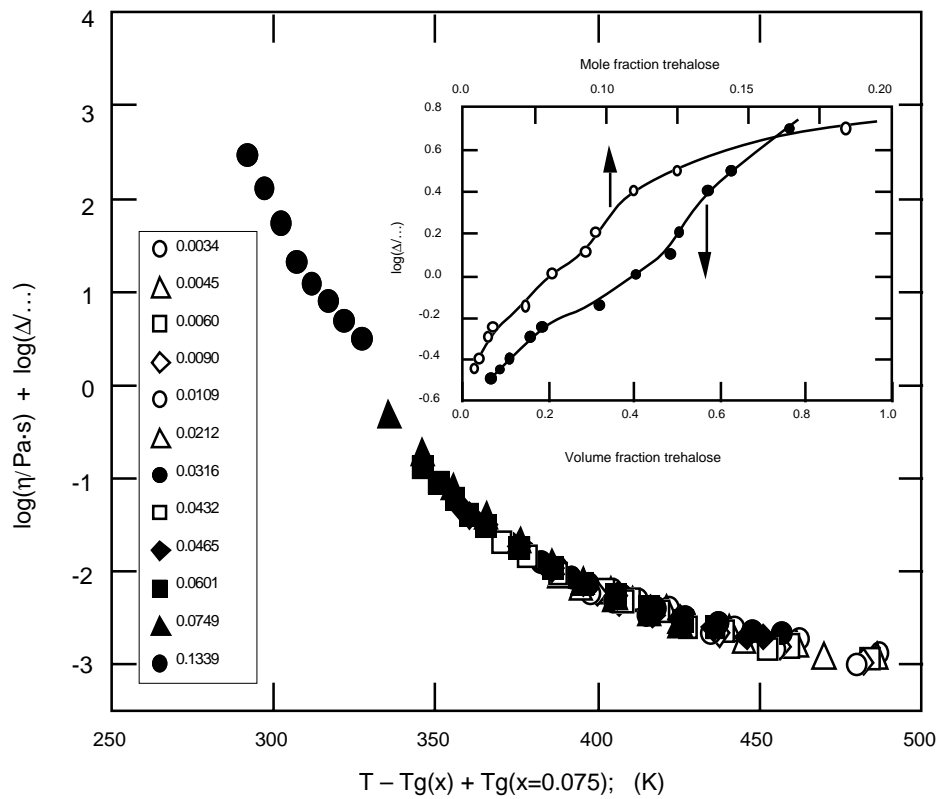
$$T_g = \frac{x_2 T_{g;2} + k(1 - x_2) T_{g;1}}{x_2 + k(1 - x_2)}$$

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

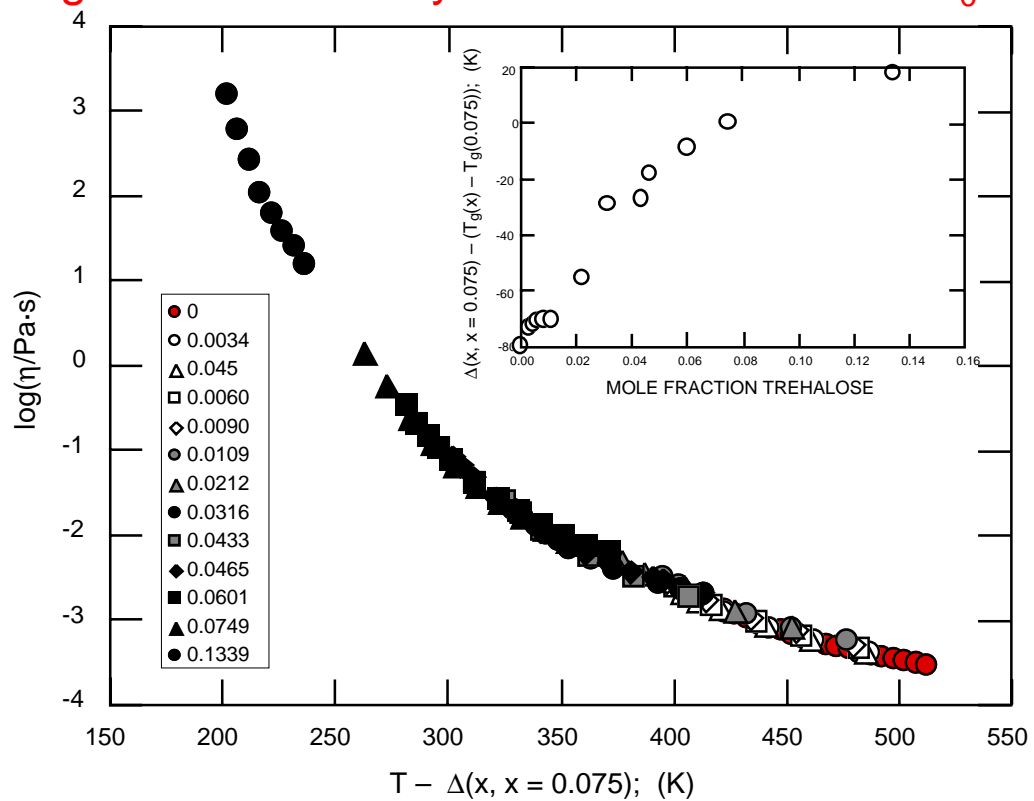
Two examples of possible correlations will be discussed:

- 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 $T - T_g$:



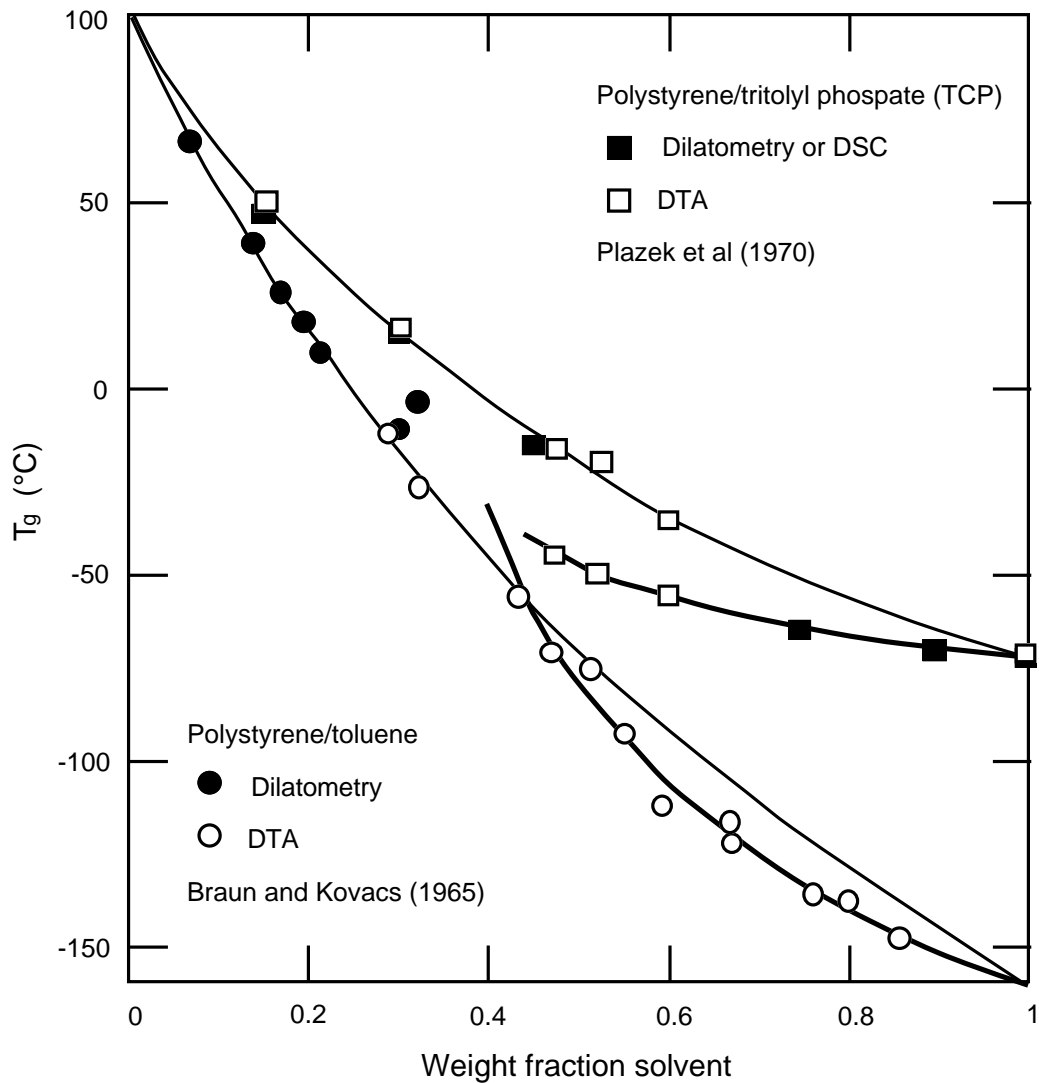
Assuming that the viscosity should scale with $T - T_0$:

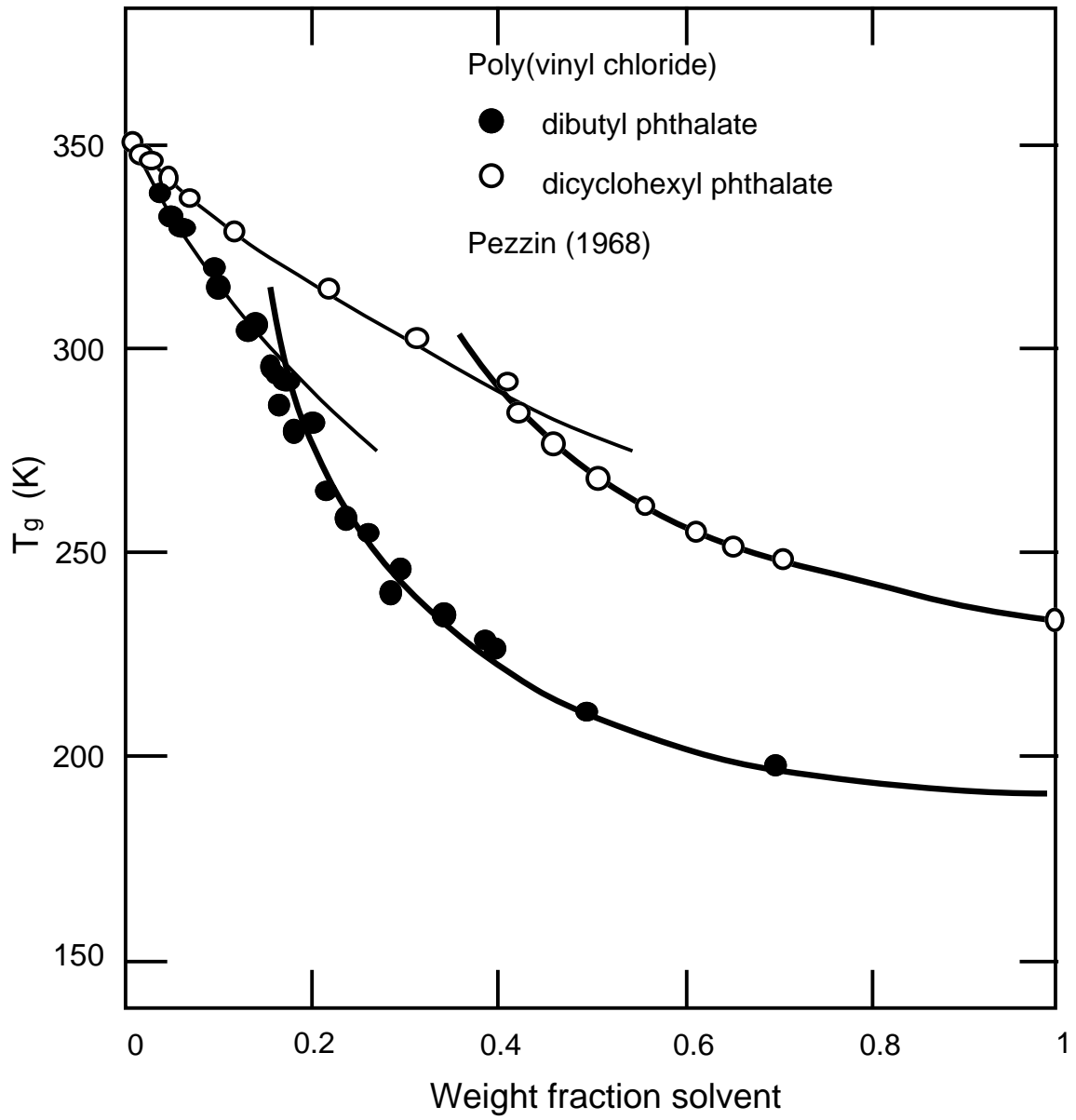


With some systems, it appears that two such expressions may be required to approximate T_g for the blend:

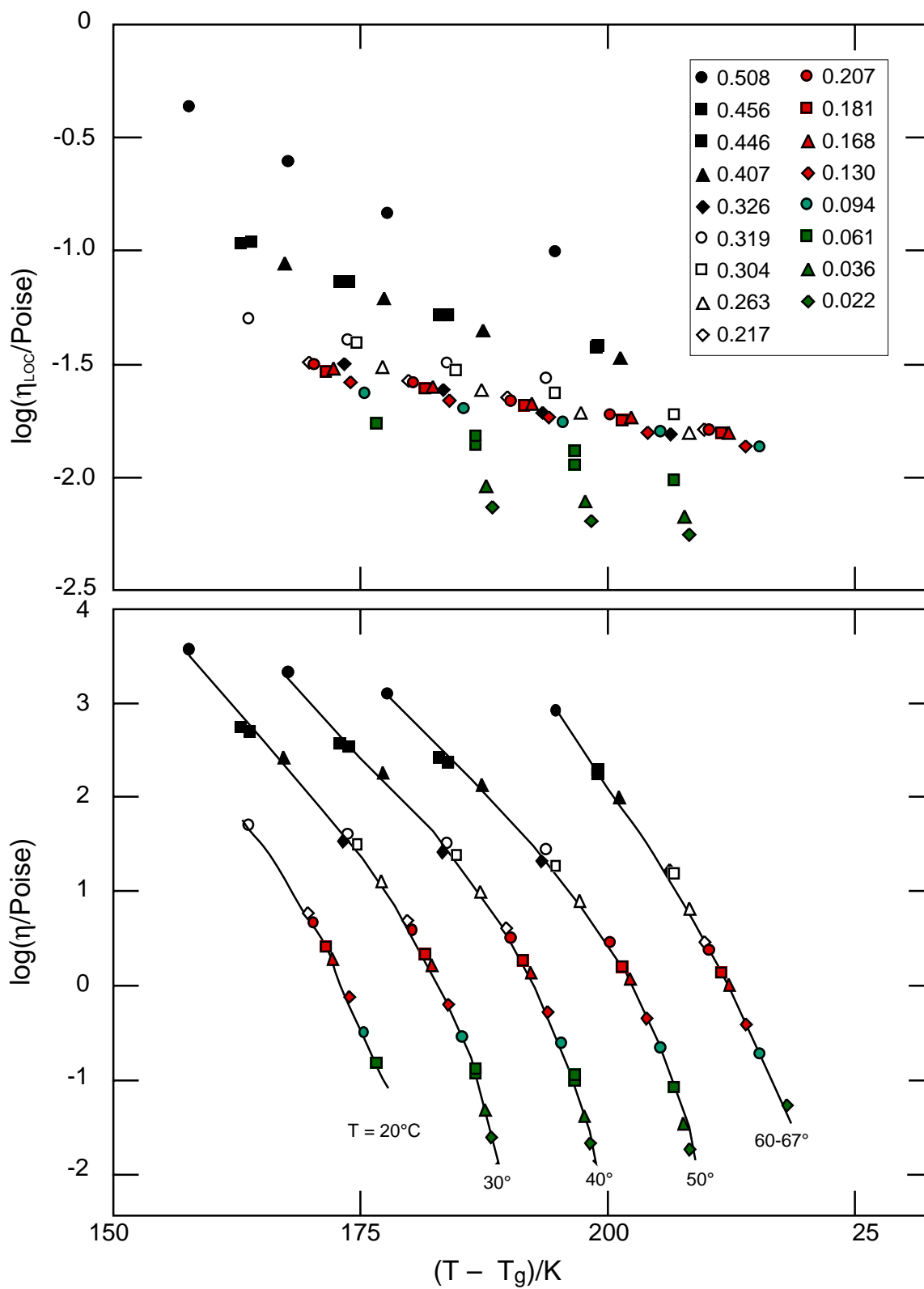
$$T_g = \text{Min} \left\{ \frac{x_2 T_{g;2} + k_1(1 - x_2) T_{g;02}}{x_2 + k_1(1 - x_2)}, \frac{x_2 T_{g;\infty 1} + k_2(1 - x_2) T_{g;1}}{x_2 + k_2(1 - x_2)} \right\}$$

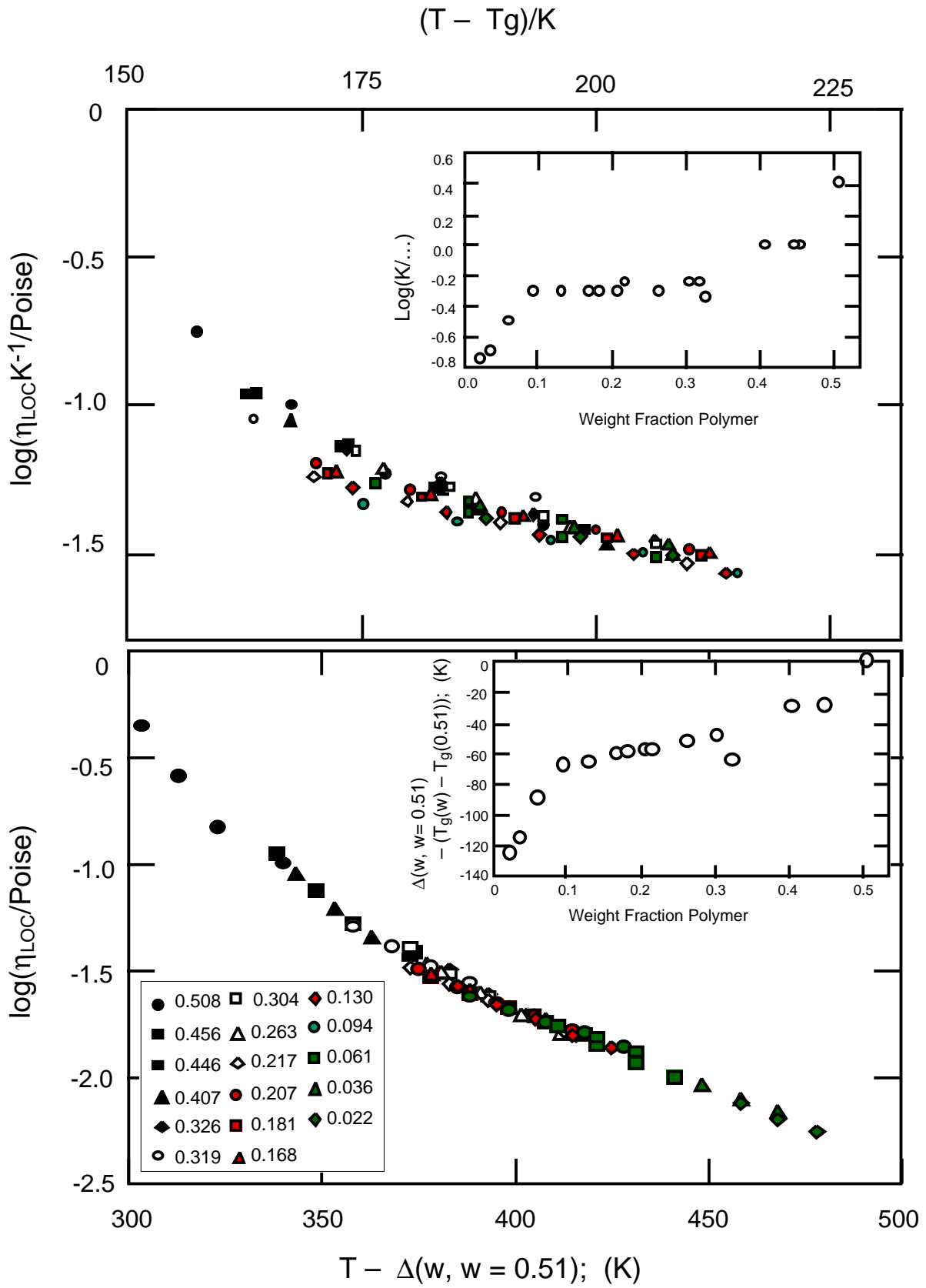
introducing additional empirical constants, and where $T_{g;2}$ for the polymer may depend approximately linearly in $1/M_n$, and.

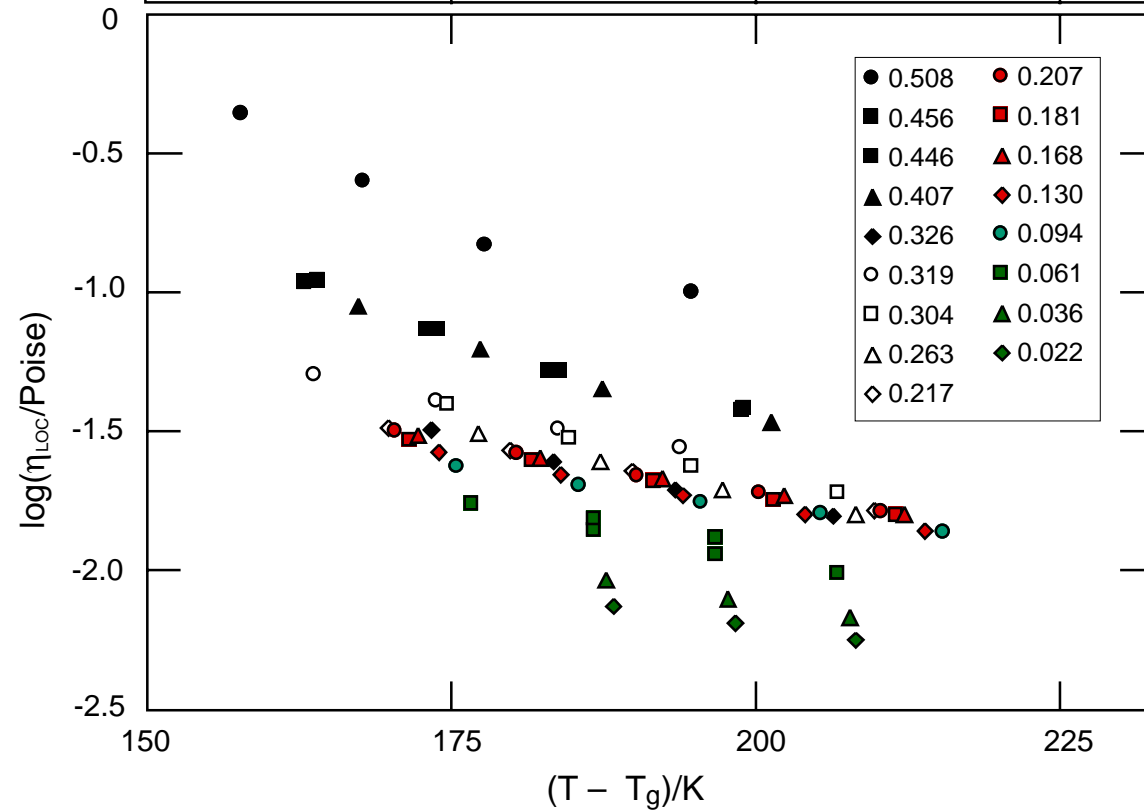
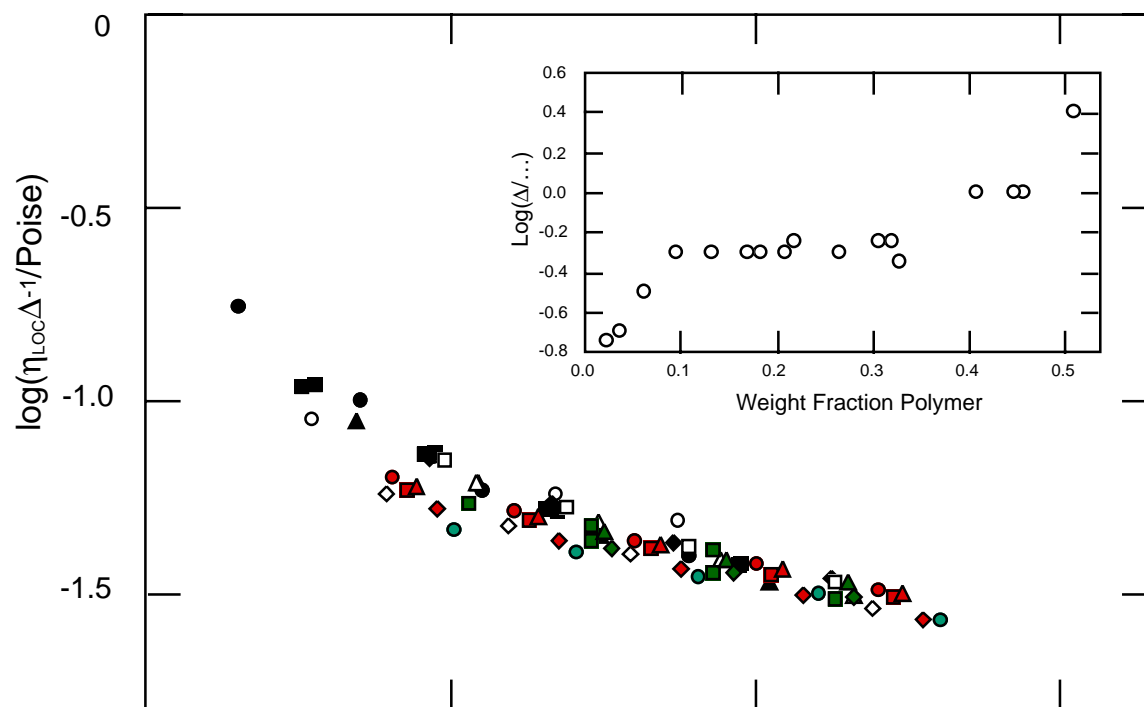




Polystyrene/styrene ($M_w = 2.4 \times 10^5$)







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

