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Weight-Average Molecular Weights from Combined Sedimentation and Viscosity Data

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LETTER TO THE EDITOR

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The combination of sedimentation coefficients s (at zero concentration) and intrinsic viscosities $[\eta]$ of unfractionated polymers according to the equations of Mandelkern and Flory (*1*) and Scheraga and Mandelkern (*2*) will normally lead to mixed averages of molecular weight. In a recent paper (*3*) one of the authors has presented a method to calculate weight average molecular weights from these data. An analogous procedure was suggested by Abe et al. (*4*), and Souček (*5*) proposed a similar method for the calculation of weight average molecular weights from sedimentation coefficients s and diffusion coefficients D of unfractionated polymers. All methods are limited to theta solutions, however. Furthermore, a discussion between the authors of the present paper has revealed that all papers failed to prove mathematically the validity of the deduced equations. The discussion has resulted at the same time in providing a proof in a more general form, i.e., for any polymer solutions. The evidence for the Flory-Mandelkern equation is presented herewith. A similar evidence exists for the Svedberg equation, including its form obtained by Souček (*5*).

Departing from the well-known equations (*1*),

$$M_i = K_{s\eta}(s_i)^{1.5}[\eta]_i^{0.5} \tag{1}$$

with

$$K_{s\eta} = \frac{N_A \eta_0}{(\Phi^{1/3} p^{-1})(1 - {}^{*}v\rho_0)} \tag{1a}$$

$$s_i = K_s M_i^{\gamma} \tag{2}$$

$$[\eta]_i = K_\eta M_i^{a} \tag{2a}$$

where M_i, s_i, and $[\eta]_i$ are molecular weight, sedimentation constant (at zero concentration), and intrinsic viscosity of an i monodisperse species of macromolecules in a polymer sample, and ${}^*v$ is the partial specific volume of the polymer in a solvent with ρ_0 its density and η_0 its viscosity; N_A and $(\Phi^{1/3}p^{-1})$ are the Avogadro and Flory-Mandelkern constants. The appropriately averaged values $\bar{s}$ and $\overline{[\eta]}$ for the sedimentation constant and intrinsic viscosity of a polymer sample are to be derived so that

$$M_w = K_{s\eta}\overline{(s)}^{1.5}\overline{[\eta]}^{0.5} \tag{3}$$

be valid. In Eq. (3), M_w is the weight average molecular weight

$$M_w = \sum_{i=1}^{i=i} w_i M_i \tag{4}$$

with

$$\sum_{i=1}^{i=i} w_i = 1 \tag{4a}$$

It is well known that the experimental value of the intrinsic viscosity, $[\eta]_{\text{exp}}$, is given by the weight average

$$[\eta]_{\text{exp}} = \sum_{i=1}^{i=i} w_i[\eta]_i \tag{5}$$

The above-mentioned $\bar{s}$ and $\overline{[\eta]}$ are assumed now to be

$$\bar{s} = K_s M_w^{\gamma} \tag{6}$$

$$\overline{[\eta]} = K_\eta M_w^{a} \tag{6a}$$

Equation (6) has been considered (3) to be a sufficient condition for satisfying Eq. (3), and a similar procedure has been used in the paper of Souček (5). Now the assumption is proved in a general form.

From Eqs. (2), (4), and (6),

$$\bar{s} = \Big(\sum_{i=1}^{i=i} w_i(s_i)^{1/\gamma}\Big)^{\gamma} \tag{7}$$

$$\overline{[\eta]} = \Big(\sum_{i=1}^{i=i} w_i[\eta]_i^{1/a}\Big)^{a} \tag{7a}$$

From Eqs. (1) and (2),

$$M_i = K_{s\eta} K_s^{1.5} K_\eta^{0.5} M_i^{1.5\gamma} M_i^{0.5a} \tag{8}$$

and analysis of the dimensions in Eq. (8) shows that the following equations must be valid:

$$K_{s\eta} K_s^{1.5} K_\eta^{0.5} = 1 \tag{9}$$

$$1.5\gamma + 0.5a = 1 \tag{10}$$

Then, from Eqs. (2) and (10),

$$[\eta]_i = (K_\eta / K_s^{(2-3\gamma)/\gamma}) s_i^{(2-3\gamma)/\gamma} \tag{11}$$

and, with Eq. (5),

$$\begin{aligned}[\eta]_{\mathrm{exp}} &= (K_\eta / K_s^{(2-3\gamma)/\gamma}) \sum_{i=1}^{i=i} w_i s_i^{(2-3\gamma)/\gamma} \\ &= (K_\eta / K_s^{(2-3\gamma)/\gamma})\, {}^{*}s \end{aligned} \tag{12}$$

if we assign

$${}^{*}s = \sum_{i=1}^{i=i} w_i s_i^{(2-3\gamma)/\gamma} \tag{13}$$

From Eqs. (7), (10), and (11),

$$\begin{aligned}\overline{[\eta]} &= (K_\eta / K_s^{(2-3\gamma)/\gamma}) \Big(\sum_{i=1}^{i=i} w_i s_i^{1/\gamma}\Big)^{(2-3\gamma)} \\ &= (K_\eta / K_s^{(2-3\gamma)/\gamma})\, \bar{s}^{(2-3\gamma)} \end{aligned} \tag{14}$$

or

$$K_\eta / K_s^{(2-3\gamma)/\gamma} = \overline{[\eta]} / \bar{s}^{(2-3\gamma)/\gamma} \tag{15}$$

From Eqs. (1) and (11),

$$\begin{aligned} M_i &= K_{s\eta} (K_\eta / K_s^{(2-3\gamma)/\gamma})^{0.5} s_i^{1.5} s_i^{(2-3\gamma)/2\gamma} \\ &= K_{s\eta} (K_\eta / K_s^{(2-3\gamma)/\gamma})^{0.5} s_i^{1/\gamma} \end{aligned} \tag{16}$$

From Eqs. (16), (4), and (7),

$$M_w = K_{s\eta} (K_\eta / K_s^{(2-3\gamma)/\gamma})^{0.5} \sum_{i=1}^{i=i} w_i s_i^{1/\gamma}$$

$$= K_{s\eta}(K_\eta/K_s^{(2-3\gamma)/\gamma})^{0.5}\bar{s}^{1/\gamma} \tag{17}$$

and, finally, with Eq. (15),

$$\begin{aligned} M_w &= K_{s\eta}\overline{[\eta]}^{0.5}(\bar{s})^{(3\gamma-2)/2\gamma}(\bar{s})^{1/\gamma} \\ &= K_{s\eta}\overline{[\eta]}\bar{s}^{1.5} \end{aligned} \tag{18}$$

i.e., the validity of Eq. (3) and thus of the assumption concerning Eq. (6) is proved.

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