A SIMPLE DERIVATION OF STAUDINGER'S RULE

By V. S. Vaidhyanathan

(*Department of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.*)

(Communicated by Dr. S. M. Shah, F.A.SC.)

Staudinger's Rule which is widely used in the viscosity method of determination of the average chain length of a polymer, states that the intrinsic viscosity of polymer solution is proportional to the average chain length of the polymer. Debye,[1] Kramers[2] and Kirkwood[3] have provided theoretical reasons for the validity of this empirical rule based on certain models. We present below a simple derivation of the above rule from the statistical mechanical theory of transport processes of a dilute polymer solution with monomer as solvent.

Bearman and Jones[4] have derived an expression for the viscosity of a non-electrolyte binary solution that

$$
\eta = \frac{c_1^2}{60 D_1} \int r \frac{dV_{11}}{dr} \psi_{11}^{*(2)} g_{11}^{(2,0)} d^3r + \frac{c_1 c_2}{15 (D_1 + D_2)}
$$

$$
\times \int r \frac{dV_{12}}{dr} \psi_{12}^{*(2)} g_{12}^{(2,0)} d^3r + \frac{c_2^2}{60 D_2}
$$

$$
\times \int r \frac{dV_{22}}{dr} \psi_{22}^{*(2)} g_{22}^{2,0)} d^3r \tag{1.1}
$$

where D_1 and D_2 are the self-diffusion coefficients of components 1 and 2 in the solution, c_1 and c_2 are the concentrations of 1 and 2, $g_{\alpha\beta}^{(2,0)}$ ($\alpha, \beta = 1, 2$) are the radial distribution functions of the corresponding equilibrium states, and $\psi_{\alpha\beta}^{*(2)}$ ($\alpha, \beta = 1, 2$) are the perturbation parameters obeying the differential equation

$$
\frac{d^2\psi_{\alpha\beta}^{*(2)}}{dr^2} + \left(\frac{d\ln g_{\alpha\beta}^{(2,0)}}{dr} + \frac{2}{r} \right) \frac{d\psi_{\alpha\beta}^{*(2)}}{dr} - \frac{6}{r^2} \psi_{\alpha\beta}^{*(2)}
$$

$$
= \frac{r \, d\ln g_{\alpha\beta}^{(2,0)}}{dr} . \tag{1.2}
$$

For the development of a molecular theory of Staudinger's rule, one needs to know the functional dependence of the perturbation parameters

$\psi_{\alpha\beta}{}^{*(2)}$ and radial distribution function $g_{\alpha\beta}{}^{(2, 0)}$ on the chain length. (Evidently $\psi_{11}{}^{*(2)}$ and $g_{11}{}^{(2, 0)}$ of the solvent-solvent interactions do not depend on the chain length of the polymer.) Application of molecular distribution functions to the polymer solutions has been carried out previously by Zimm and others,[5] in which attention has been focused mainly on polymer-polymer interactions. From their work, it appears to be difficult to derive the dependence of $g_{22}{}^{(2, 0)}$ and $\psi_{22}{}^{*(2)}$ on the chain length. However, it turns out that this knowledge about polymer-polymer interactions is not necessary to justify Staudinger's rule (in the limit of dilute polymer solutions). But we need to know the functional dependence of $g_{12}{}^{(2, 0)}$ and $\psi_{12}{}^{*(2)}$ on the chain length of the polymer. Explicitly, we need considerations of the polymer-solvent interactions.

STATISTICAL MECHANICAL THEORY

We consider a system of two components containing $(N_1 + N_2)$ molecules which are not chemically reacting. We label the solvent component of monomers by 1 and label the polymer component by 2. The polymer is supposed to be made up of monomer units identical with the solvent molecules. Let the average chain length of the polymer be M. We assume that the interactions between polymer segments and monomers to be of short range of the order of intermolecular separation and that the segments are connected by completely flexible joints (random flight model). In other words, we assume that the monomer segments of the polymer are essentially identical with the solvent molecules, except that they are linked together with other monomer units of the polymer.

We denote the position of the solvent molecule i by the vector $\vec{R}_{1i}$ and its momentum by $\vec{P}_{1i}$. We denote the position of the polymer segment k by the vector $\vec{R}_{2\beta k}$ and its momentum by $\vec{P}_{2\beta k}$. The space of a single polymer of chain length M is equivalent to the multi-dimensional hyperspace of M monomer units or solvent molecules. Thus, the pair distribution functions of the solvent-polymer interactions are equivalent to the distribution function of $(M + 1)$-th order of the phase space defining only solvent-polymer segment interactions. The solvent molecules and the monomer units are assumed to interact according to the laws of classical mechanics and hence the time-smoothed probability distribution function:

$$f^{(N_1 + MN_2)}\left(\vec{R}_{11}, \vec{R}_{12} \cdots, \vec{R}_{2\beta N_2}, \vec{P}_{11}, \vec{P}_{12} \cdots, \vec{P}_{2\beta N_2}; \ t\right)$$

at a time t in a statistical ensemble obeys Liouville's equation

$$\frac{\partial f^{(N_1+MN_2)}}{\partial t} + \sum_{\gamma=1}^{2} \sum_{i=1}^{N\gamma} \frac{\vec{P}_{\gamma i}}{m_\gamma} \nabla_{\vec{R}_{\gamma i}} f^{(N_1+MN_2)}$$

$$+ \sum_{\gamma=1}^{2} \sum_{i=1}^{N\gamma} \nabla_{\vec{R}_{\gamma i}} U \cdot \nabla_{\vec{P}_{\gamma i}} f^{(N_1+MN_2)} = 0 \qquad (2.1)$$

where U is the total potential energy of the entire system. Equation (2.1) is permissible because of the assumptions of completely flexible joints, short range intermolecular forces and random flight model.

The expectation value at a time t of a dynamical variable

$$\phi\left(\vec{R}_{11}, \vec{R}_{12}, \vec{R}_{2\beta N_2}, \vec{P}_{11} \cdots, \vec{P}_{2\beta N_2}\right)$$

may be written as $\langle \phi; f^{(N)} \rangle$ where by definition

$$\langle \phi; f^{(N)} \rangle = \int \phi f^{(N)} d^3\vec{R}_{11} \cdots d^3\vec{R}_{2MN_2} d^3\vec{P}_{11} \cdots, d^3\vec{P}_{2MN_2},$$

with

$$N \equiv N_1 + MN_2. \qquad (2.2)$$

If we define the microscopic particle densities in the singlet space of solvent molecules and polymer segments,

$$\gamma_a^{(1)} = \sum_{i=1}^{N_a} \delta\left(\vec{R}_{ai} - \vec{r}_1\right) \delta\left(\vec{P}_{ai} - \vec{p}_1\right) \qquad (2.3)$$

where $\delta\left(\vec{R}_{ai} - \vec{r}_1\right)$ and $\delta\left(\vec{P}_{ai} - \vec{p}_1\right)$ are the appropriate Dirac delta functions, then the average densities in the singlet space (of polymer segments) are given by[6]

$$\omega_a^{(1)} = \langle \gamma_a^{(1)}; f^{(N)} \rangle. \qquad (2.4)$$

We express the mean particle concentration c_a of molecules of the solvent at a point $\vec{r}_1$ the relation

$$c_a\left(\vec{r}_1\right) = \int \omega_a^{(1)}\left(\vec{r}_1 \vec{p}_1\right) d^3\vec{p}_1. \qquad (2.5)$$

Similarly, the mean particle concentration c_β of the monomer segments of the polymer at a point $\vec{r}_2$ can be defined by

$$c_\beta\left(\vec{r}_2\right) = \int \omega_a{}^{(1)}\left(\vec{r}_2 \cdot \vec{p}_2\right) d^3\vec{p}_2.$$ (2.6)

where

$$\gamma_\beta{}^{(1)} = \sum_{K=1}^{MN_2} \delta\left(\vec{R}_{2\beta K} - \vec{r}_2\right)\delta\left(\vec{P}_{2\beta K} - \vec{p}_2\right).$$ (2.7)

The microscopic particle densities in the singlet space of the polymer 2 is given by the M dimensional hyperspace particle densities of the segments and hence

$$\gamma_2{}^{(1)} = \sum_{K=1}^{MN_2} \prod_{\beta=1}^{M} \delta\left(\vec{R}_{2\beta K} - \vec{r}_2\right)\delta\left(\vec{P}_{2\beta K} - \vec{p}_2\right).$$ (2.8)

The mean particle concentration in the singlet space of the polymer is given by

$$\begin{aligned}
c_2{}^{(1)} &= \int \omega_2{}^{(1)}\left(\vec{r}_1 \cdots \vec{r}_M \vec{p}_1 \cdots \vec{p}_M\right) d^3\vec{p}_1 \cdots d^3\vec{p}_M \\
&= \int \omega_\beta{}^{(M)}\left(\vec{r}_1 \cdots \vec{r}_{MJ}\vec{p}_J \cdots \vec{p}_M\right) d^3\vec{p}_1 \cdots d^3\vec{p}_M \\
&= c^{(M)}{}_{\beta_1 \cdots \beta_M}.
\end{aligned}$$ (2.9)

The singlet space concentration of the polymer $c_2{}^{(1)}$ corresponds to the M dimensional space concentration of the monomer units and thus,

$$c_2{}^{(1)} = M c_\beta{}^{(1)} ;$$ (2.10)

because, the probability of observing a polymer in its singlet space is equivalent to the probability of observing the polymer segments in M locations simultaneously and is equal to the sum of the probabilities of observing each segment in a given location. Defining $\langle c_\beta{}^{(1)}\rangle$ to be the weighted average of these individual probabilities one can state that $c_2{}^{(1)} = M \langle c_\beta{}^{(1)}\rangle$. Physically, one can argue that the presence of a single polymer chain is equivalent to the presence of M polymer segments.

In the configuration of ordered pairs of monomer molecules, the average number density $c_{\alpha\beta}{}^{(2)}$ of monomer molecule α at $\vec{r}_1$ and polymer segment β at $\vec{r}_2$ is defined by the relation[6]

$$c_{\alpha\beta}{}^{(2)} \left(\vec{r}_1 \cdot \vec{r}_2 \right) = \int \omega_{\alpha\beta}{}^{(2)} \left(\vec{r}_1 \vec{r}_2 \cdot \vec{p}_1 \vec{p}_2 \right) d^3 \vec{p}_1 d^3 \vec{p}_2 \qquad (2.11)$$

where the average number density in pair space of the solvent molecules is

$$\omega_{\alpha\beta}{}^{(2)} = \langle \gamma_{\alpha\beta}{}^{(2)}; f^{(N)} \rangle \qquad (2.12)$$

and $\gamma_{\alpha\beta}{}^{(2)}$ is defined by the equation

$$\gamma_{\alpha\beta}{}^{(2)} = \sum_{i=1}^{N_1} \sum_{j=1}^{MN_2} \delta \left(\vec{R}_{\alpha i} - \vec{r}_1 \right) \delta \left(\vec{P}_{\alpha i} - \vec{p}_1 \right) \delta \left(\vec{R}_{\beta j} - \vec{r}_2 \right)$$

$$\times \delta \left(\vec{P}_{\beta j} - \vec{p}_2 \right). \qquad (2.13)$$

The average number density $c_{12}{}^{(2)}$ of a monomer molecule α at $\vec{r}_1$ and a polymer molecule 2 at $\vec{r}_2, \vec{r}_3, \cdots, \vec{r}_{M+1}$ is defined by the relation

$$c_{12}{}^{(2)} \left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots, \vec{r}_{M+1} \right)$$

$$= \int \omega_{12}{}^{(2)} \left(\vec{r}_1, \cdots, \vec{r}_{M+1} \vec{p}_1 \cdots \vec{p}_{M+1} \right) d^3 \vec{p}_1 \cdots, d^3 \vec{p}_{M+1} \qquad (2.14)$$

where the average number density is defined by

$$\omega_{12}{}^{(2)} = \langle \gamma_{12}{}^{(2)}; f^{(N)} \rangle \qquad (2.15)$$

and $\gamma_{12}{}^{(2)}$ is defined by the equation

$$\gamma_{12}{}^{(2)} = \sum_{i=1}^{N_\alpha} \sum_{k=1}^{MN_2} \prod_{\beta=1}^{M} \delta \left(\vec{R}_{\alpha i} - \vec{r}_1 \right) \delta \left(\vec{P}_{\alpha i} - \vec{p}_1 \right) \delta \left(\vec{R}_{\beta K} - \vec{r}_j \right)$$

$$\times \delta \left(\vec{P}_{\beta K} - \vec{p}_j \right) \qquad j = 2 \cdots (M + 1). \qquad (2.16)$$

Thus, the pair space polymer-solvent concentrations is given by

$$c_{12}{}^{(2)} = c_{\alpha\beta}{}^{(2)} M \qquad (2.17)$$

where $c_{\alpha\beta}{}^{(2)}$ refers to the pair space solvent-polymer segment concentration. The pair correlation functions $g_{11}{}^{(2, 0)}$ and $g_{12}{}^{(2, 0)}$ are defined by the relations,

$$c_{11}{}^{(2)} = c_1{}^2 g_{11}{}^{(2, 0)}$$

$$c_{12}{}^{(2)} = c_1 c_2 g_{12}{}^{(2, 0)}. \qquad (2.18)$$

Therefore we have

$$c_{12}^{(2)} = c_1 c_\beta M g_{12}^{(2,\ 0)}$$

$$c_{1\beta}^{(2)} = c_{11}^{(2)} = c_1 c_\beta g_{12}^{(2,\ 0)}$$

(because of the assumptions)   (2.19)

and thus we obtain

$$g_{12}^{(2,\ 0)} = \frac{g_{11}^{(2,\ 0)}}{M} \qquad (2.20)$$

where $g_{11}^{(2,\ 0)}$ refers to the solvent-solvent interactions and $g_{12}^{(2,\ 0)}$ to the solvent-polymer interactions. A physical explanation can be given for the last result. When interactions are of short range and somewhat akin to a cut-off potential, $g_{12}^{(2,\ 0)}$ which defines the probability of observing a polymer molecule at a specified distance from a monomer molecule, which is located within the interaction range will be the sum of the probabilities that all the M polymer segments are within this field of interaction. Thus, we arrive at the plausible result that $g_{11}^{(2,\ 0)}$ for the solvent-solvent interactions is equal to chain length times $g_{12}^{(2,\ 0)}$ for the polymer-solvent pair correlation functions. *It should be noted that the above result is by no means rigorous and the application of equation (1.1) to polymer solutions is to be justified on the basis of a more exact theory.* For our consideration, we assume that equation (1.1) is applicable to dilute polymer solutions obeying the assumptions of flexible joints and random flight model.

The perturbation parameter $\psi_{12}^{*(2)}$ obeys the differential equation (1.2) and since the equation involves only the variable r, it follows that $\psi_{12}^{*(2)}$ must also be a linear function in chain length. Thus we have

$$\psi_{12}^{*(2)} = \frac{\psi_{11}^{*(2)}}{M} \ . \qquad (2.21)$$

INTRINSIC VISCOSITY

The intrinsic viscosity $[\eta]$ of a dilute polymer solution is defined by the relation

$$[\eta] = \left[\frac{\eta_{sp}}{c_2}\right]_{lim\ c_2 \to 0} = \left(\frac{\eta_r - 1}{c_2}\right)_{c_2 \to 0} \qquad (3.1)$$

where η_{sp} is the specific viscosity and η_r the relative viscosity of the solution relative to the viscosity of the pure solvent. We shall define the functions $K(r)$ and $L(r)$ by the relations

$$g_{12}^{(2,\,0)} = K(r) M$$
$$\psi_{12}^{*(2)} = L(r) M \tag{3.2}$$

where $K(r)$ and $L(r)$ are not functions of the chain length.

Assuming that equation (1.1) is applicable to dilute polymer solutions with completely flexible joints and random motion segment polymer molecules the viscosity of the binary polymer solution can be written as

$$\eta = \frac{c_1^2}{60D_1} A_{11} + \frac{c_1 c_2}{15(D_1 + D_2)} A_{12} + \frac{c_2^2}{60D_2} A_{22}$$

where

$$A_{iK} = \int r \frac{dV_{iK}}{dr} \psi_{iK}^{*(2)} g_{iK}^{(2,\,0)} d^3\vec{r}. \tag{3.3}$$

The viscosity of the pure solvent is given by

$$\eta_{11}^0 = \frac{c_1^{02}}{60D_1^0} A_{11} \tag{3.4}$$

where c_1^0 and D_1^0 are the concentration and self-diffusion coefficient of the solvent in pure state.

Thus, the equation for the relative viscosity of the solution is given by

$$\eta_r = \frac{\eta}{\eta_{11}^0} = \frac{c_1^2 D_1^0}{c_1^{02} D_1} \frac{A_{11}}{A_{11}^0} + \frac{4c_1 c_2 D_1^0}{c_1^{02}(D_1 + D_2)} \frac{A_{12}}{A_{11}^0}$$
$$+ \frac{c_2^2}{c_1^{02}} \frac{D_1^0}{D_2} \frac{A_{22}}{A_{11}^0} \tag{3.5}$$

and the expression for the specific viscosity is

$$\eta_{sp} = \frac{c_1^2 D_1^0}{c_1^{02} D_1} \frac{A_{11}}{A_{11}^0} - \frac{c_1^{02} D_1 A_{11}^0}{c_1^{02} D_1 A_{11}^0} + \frac{4c_1 c_2 D_1^0}{c_1^{02}(D_1 + D_2)} \frac{B_{12} M^2}{A_{11}^0}$$
$$+ \frac{c_2^2 D_1^0}{c_1^{02} D_2} \frac{A_{22}}{A_{11}^0}$$

where

$$B_{12} = \int r \frac{dV_{12}}{dr} K(r) L(r) d^3\vec{r}. \tag{3.6}$$

Since the polymer is made up of M monomer units identical with the solvent molecules, one could assume with negligible error that

$$D_1 = MD_2. \tag{3.7}$$

If the assumptions of regular solution theory are applicable, it follows from Bearman's results[5] that

$$\frac{D_1}{D_2} = \frac{v_2}{v_1} = M, \tag{3.8}$$

where v_1 and v_2 are the molar volumes of the solvent and polymer respectively.

Introducing the results of equation (3.7) in (3.6), and considering the limit when c_2, the concentration of polymers, tends to zero, the expression for the specific viscosity becomes

$$(\eta) = KM \tag{3.9.}$$

which is Staudinger's rule, where K is a constant independent of the chain length. For systems with solvents other than the monomer, one could incorporate a correction factor α to partly overcome the assumptions made, to derive the relation

$$(\eta) = KM^\alpha \tag{3.10}$$

which expression is widely used in polymer chain length determinations.[7]

The author wishes to acknowledge fruitful discussions with Professor Richard J. Bearman.

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