# Intrinsic Viscosity of Rigid Complex Molecules[*1]

Keishiro Tsuda

*Textile Research Institute of Japanese Government, Kanagawa-ku, Yokohama*

(Received December 16, 1968)

The intrinsic viscosity of a molecule consisting of $n$ elements is expressed in terms of the hydrodynamic force $\boldsymbol{F}_l$ exerted on solvent by an element $l$ as[1]

$$[\eta] = -\frac{\boldsymbol{N}_0}{M\eta_0\dot{\varepsilon}}\sum_{l=1}^{n}\langle(\boldsymbol{F}_l\cdot\boldsymbol{e}_x)(\boldsymbol{R}_l\cdot\boldsymbol{e}_y)\rangle. \tag{1}$$

Here $\boldsymbol{N}_0$ is the Avogadro number, $M$ the molecular weight of the solute, $\eta_0$ the solvent viscosity, $\dot{\varepsilon}$ the rate of strain, and $\boldsymbol{R}_l$ the position of the indicated element $l$ relative to the molecular center of mass. $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$ are the unit vectors in the $x$ and $y$ directions, respectively. Hence, the unperturbed velocity of the solvent at the point $\boldsymbol{R}_l$ is defined by

$$\boldsymbol{v}_l{}^0 = \dot{\varepsilon}(\boldsymbol{R}_l\cdot\boldsymbol{e}_y)\boldsymbol{e}_x. \tag{2}$$

The hydrodynamic force $\boldsymbol{F}_l$ is then written as

$$\boldsymbol{F}_l = -\zeta(\boldsymbol{v}_l{}^0 - \boldsymbol{u}_l) - \zeta\sum_{s=1}^{n}{}'\boldsymbol{T}_{ls}\cdot\boldsymbol{F}_s, \tag{3}$$

where $\zeta$ is the friction constant of a single element, $u_l$ the velocity of element $l$, and the sum extends over 1 to $n$, but $l$, with respect to $s$. $\boldsymbol{T}_{ls}$ represents the Oseen interaction tensor which is defined by

$$\boldsymbol{T}_{ls} = \frac{1}{8\pi\eta_0\boldsymbol{R}_{ls}}\left(\boldsymbol{I} + \frac{\boldsymbol{R}_{ls}\boldsymbol{R}_{ls}}{R_{ls}{}^2}\right), \tag{4}$$

where $R_{ls}$ is the distance between elements $l$ and $s$.

For a solute molecule of rigid structure, we have

$$\boldsymbol{u}_l = (\dot{\varepsilon}/2)[(\boldsymbol{R}_l\cdot\boldsymbol{e}_y)\boldsymbol{e}_x - (\boldsymbol{R}_l\cdot\boldsymbol{e}_x)\boldsymbol{e}_y]. \tag{5}$$

Equation (3) may then be rewritten in the form

$$\boldsymbol{F} = -(\dot{\varepsilon}/2)\zeta a_\beta - \zeta\boldsymbol{T}\cdot\boldsymbol{F}, \tag{6}$$

or in its equivalent form,

$$-(1/\dot{\varepsilon})\boldsymbol{a}_\alpha\cdot\boldsymbol{F} = (\zeta/2)g_{\alpha\beta} + (\zeta/\dot{\varepsilon})\sum_{\nu}\boldsymbol{a}_\alpha\boldsymbol{a}^\nu\boldsymbol{T}\boldsymbol{a}_\nu\boldsymbol{F}, \tag{7}$$

with the abbreviations,

$$\begin{aligned}
&\boldsymbol{F} = \sum_l\boldsymbol{F}_l, \quad \boldsymbol{T} = \sum_l\sum_s\boldsymbol{T}_{ls},\\
&\boldsymbol{a}_\beta = \sum_l[(\boldsymbol{R}_l\cdot\boldsymbol{e}_x)\boldsymbol{e}_y + (\boldsymbol{R}_l\cdot\boldsymbol{e}_y)\boldsymbol{e}_x],\\
&\boldsymbol{a}_\alpha = \sum_l(\boldsymbol{R}_l\cdot\boldsymbol{e}_y)\boldsymbol{e}_x, \quad g_{\alpha\beta} = \boldsymbol{a}_\alpha\cdot\boldsymbol{a}_\beta.
\end{aligned} \tag{8}$$

Further, Eq. (7) is transformed to

$$\eta_{\alpha\beta} = (1/2)\zeta g_{\alpha\beta} - \zeta\sum_{\nu}T_\alpha{}^\nu\eta_{\nu\beta} \tag{9}$$

with

$$\begin{aligned}
\eta_{\alpha\alpha} &= -(\zeta\boldsymbol{a}_\alpha/\dot{\varepsilon})[-(\dot{\varepsilon}/2)\boldsymbol{a}_\alpha - \boldsymbol{T}\cdot\boldsymbol{F}],\\
\eta_{\alpha\beta} &= -(\zeta\boldsymbol{a}_\alpha/\dot{\varepsilon})[-(\dot{\varepsilon}/2)\boldsymbol{a}_\beta - \boldsymbol{T}\cdot\boldsymbol{F}],\\
\eta_{\beta\alpha} &= -(\zeta\boldsymbol{a}_\beta/\dot{\varepsilon})[-(\dot{\varepsilon}/2)\boldsymbol{a}_\alpha - \boldsymbol{T}\cdot\boldsymbol{F}],\\
\eta_{\beta\beta} &= -(\zeta\boldsymbol{a}_\beta/\dot{\varepsilon})[-(\dot{\varepsilon}/2)\boldsymbol{a}_\beta - \boldsymbol{T}\cdot\boldsymbol{F}].
\end{aligned} \tag{10}$$

Multiplying Eq. (9) by $g^{\gamma\alpha}$, summing the result over $\alpha$, and using the relation,

$$\sum_{\alpha}(\eta^{-1})^{\gamma\alpha}\eta_{\alpha\beta} = \delta_\beta^\gamma, \tag{11}$$

we obtain

$$(1/2)(\eta^{-1})^{\alpha\beta} = (g^{\alpha\beta}/\zeta) + T^{\alpha\beta}. \tag{12}$$

Substituting Eq. (12) into Eq. (1), and taking the average over all possible orientations of the solute molecule, we obtain

$$\begin{aligned}
[\eta] &= (\boldsymbol{N}_0/M\eta_0)\langle\eta_{\alpha\beta}\rangle\\
&= \frac{\boldsymbol{N}_0}{6M\eta_0}\left(\sum_{l=1}^{n}\zeta R_l{}^2\right)\Biggl\{1 + \frac{\zeta}{8\pi\eta_0\sum\limits_{l=1}R_l{}^2}\sum_{l=1}^{n}\sum_{s=1}^{n}\biggl\{\frac{R_lR_s\cos\alpha_{ls}}{R_{ls}}\\
&\quad + \frac{1}{10R_{ls}{}^3}[4R_lR_s(R_l{}^2 + R_s{}^2)\cos\alpha_{ls}\\
&\quad - R_l{}^2R_s{}^2(1 + 7\cos^2\alpha_{ls})]\biggr\}\Biggr\}
\end{aligned} \tag{13}^{*1}$$

with

$$|\boldsymbol{R}_l| = R_l, \ |\boldsymbol{R}_s| = R_s, \ (\boldsymbol{R}_l\cdot\boldsymbol{R}_s) = R_lR_s\cos\alpha_{ls}. \tag{14}$$

Let us now show some results obtained by applying the so-called *shell model*[2] in evaluation of Eq. (13). The first example is a spherical molecule of radius $r$, whose surface is covered by a number of small spherical elements being in contact with one another. In the limit that the number of small elements approaches infinity while their size tends to zero, the above Eq. (13) yields the Einstein equation,

$$[\eta] = (5\boldsymbol{N}_0/2M)(4\pi r^3/3). \tag{15}$$

The second example is a tetrahedral contact arrangement of four identical spheres which may be regarded as a model of hemoglobin molecule. Thus each sphere may be regarded as a myoglobin molecule. The shell model calculation of Eq. (13) yields

$$[\eta](\text{hemo})/[\eta](\text{myo}) = 1.28. \tag{16}$$

This result is to be compared with the experimental values of $[\eta]$, 4 and 3.6 (cc/g) for hemoglobin,[3,4] and 3 (cc/g) for myoglobin.[3] The agreement between theory and experiment seems satisfactory.

More details of the theory will be published later with various applications to other biopolymers and flexible chain polymers.

---

[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, April 1968, Osaka.

[1] J. Riseman and J. G. Kirkwood, *"Rheology,"* Vol. 1, ed. by F. R. Eirich, Academic Press, Inc. New York (1956), p. 495.

[2] V. Bloomfield, W. O. Dalton and K. E. Van Holde, *Biopolymers*, **5**, 135 (1967).

[3] R. F. Steiner, "The Chemical Foundation of Molecular Biology" Van Nostrand, Princeton N. J. (1965), Chap. 6, V. Table 6–2.

[4] C. Tanford, "Physical Chemistry of Macromolecules" John Wiley, New York (1961), p. 394.