On the Configuration of Chain Molecules. II.

The effect of intramolecular interaction on the apparent volume of the flexible long-chain molecule.*

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1. The standard state.

The configuration of the long chain molecule is a very important factor deciding the physical properties of its solution such as viscosity, diffusion, sedimentation velosity, etc.

If the parts of the chain have the tendency to bend irregularly, the long chain shows various configurations like the traces of a Brownian particle. The distance r of the both ends of such a molecule has the mean value

$$\langle r^2 \rangle = b^2 a^2 n \tag{1}$$

where a is the length of an element of the chain, n is the number of the elements, and b is the constant showing flexibility. The value b^2 is 1 for the independently flexible elements, 2 for the free rotation model of paraffine, and about 6 for the hindered rotation model of it. The distribution probability of r is also known, but r expresses insufficiently the degree of 3-dimensional extension of the molecule. (Fig. 1).

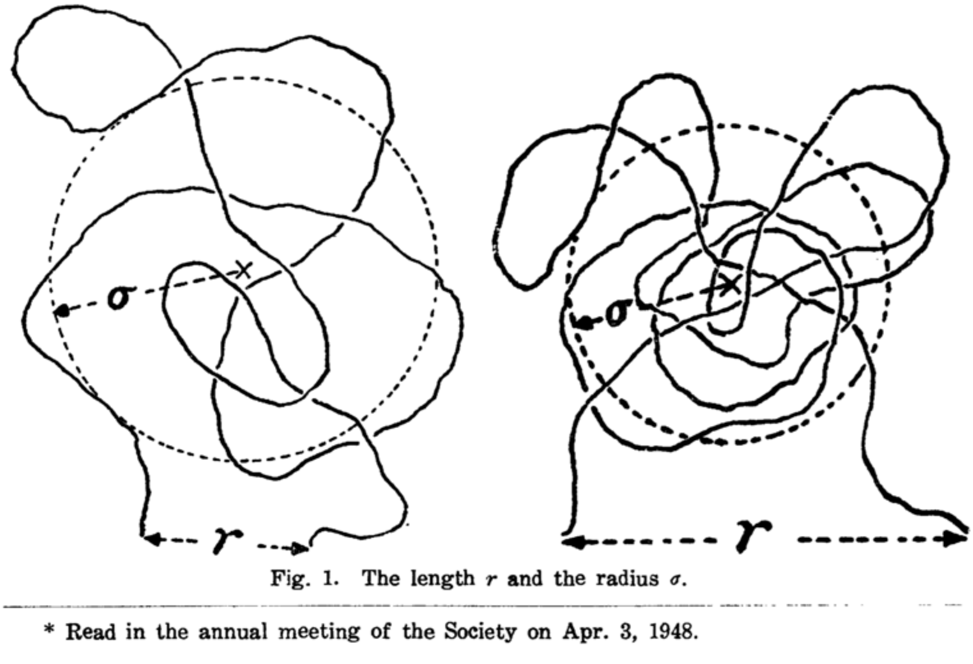

Fig. 1. The length r and the radius σ.

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* Read in the annual meeting of the Society on Apr. 3, 1948.

Next, we take up 'the radius of gyration' for this purpose. Let $r_1, r_2, \ldots, r_i, \ldots$ be the distances of elements from the centre of mass, σ is defined by the formula

$$\sum r_i^2 = 3n\sigma^2 \tag{2}$$

The mean square value of the radius of gyration of ordinary use around the axis through the centre of mass is equal to $2n\sigma^2$. σ_0, the square root of the mean value of the square of σ, for the molecule above shown, is given by the equation

$$\sigma_0^2 = \langle\sigma^2\rangle = \langle r^2\rangle/18^{(1)(2)} \tag{3}$$

and the distribution of σ is in the similar type to that of r:

$$A\sigma^2 \exp(-\alpha\sigma^2)d\sigma, \text{ where } A = 4\sqrt{\alpha^3/\pi},\ \alpha = 3/2\sigma_0^2 = 27/b^2a^2n \tag{4}$$

The state in which equations (1), (3) and (4) are correct is now named as the standard state.

2. The solvation energy.

These properties of the standard state have been derived on the assumption that there are no forces between the elements of the chain apart from each other on the chain. But however apart along the chain the elements near enough in the space can affect each other. If the energy of contact of the element is high, the molecule is apt to take the more extended configurations, and if low, the less extended. We shall discuss the effect of this energy on average values of σ, the quantity expressing the apparent volume of the molecule.

If the chain molecule is surrounded by other molecule of the same species, for example one of the isoprene polymers in rubber block, many of the elements of the chain may have no contact with any other elements of 'this' molecule, but must always be in contact with some other elements of 'other' molecules of the 'same' nature. Therefore the energy is independent of the contact of two parts of a molecule, and the ideal equations (1), (3) and (4) are correct. The condition is similar in the case where the surrounding molecules are separated into shorter chains. Thus we can say that there is no effect of the intramolecular attraction or repulsion in the solvents of the homologous series of the chain molecule, e. g. polyethylene in the solvents of paraffine series.

In other solvents the contacts are accompanied by some excess of energy, positive or negative. And the distribution is dominant in the

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(1) K. Suzuki, this Bulletin, **20** (1947), 19.

(2) P. Debye, *J. Chem. Phys.*, **14** (1946), 636.

states of lower energy than those of higher energy, and the averages of σ will differ from those of the standard state.

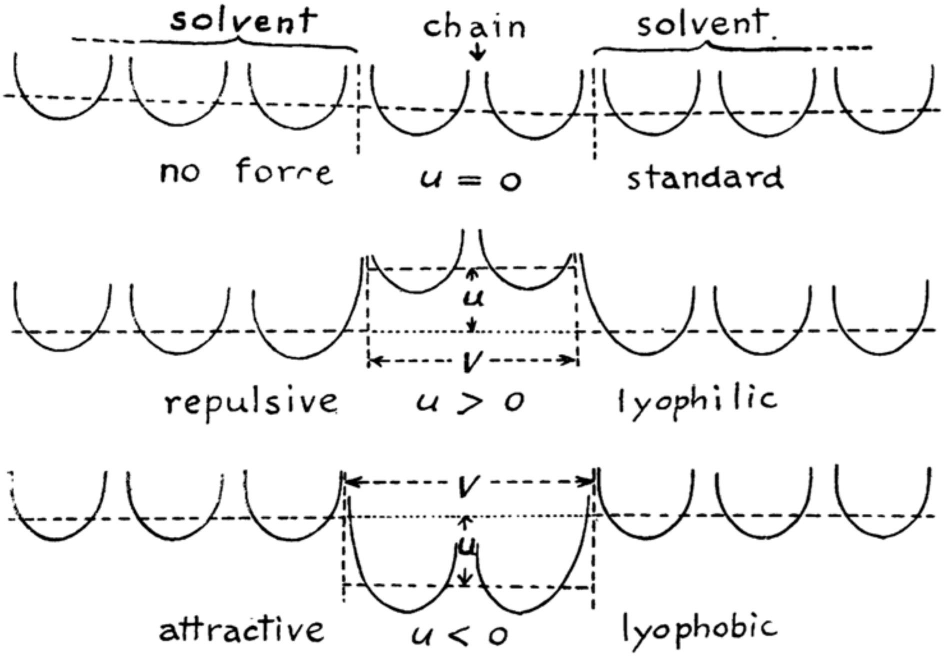

Fig. 2. Potential energy of an element of the chain in the neighbourhood of another element. u : contact energy. v : contact range.

The difference of energy due to the removal from the molecules of the same kind and the contact with solvent molecules is called 'solvation energy' and is the important factor which decides the apparent volume.

3. Contact number.

If an element is in the small volume v in the neighbourhood of another element, we consider that these elements are in contact with each other and have excess energy u compared with other two elements which are apart from each other and surrounded by solvent molecules.

The number of contacts f of this kind within a molecule must be given by the formula

$$f \propto v n^2 \sigma^{-3}$$

This proportional constant is estimated as follows: the distribution probability of an element of a molecule of the given σ in the volume element $dxdydz$ in the Cartesian coordinate system with the origin at the centre of mass is

$$p dxdydz = (\sqrt{2\pi}\sigma)^{-3} \exp\{-(x^2+y^2+z^2)/2\sigma^2\} dxdydz \tag{5}$$

The probability that another element is in the small volume v in the neighbourhood of the first is pv. The number of combinations of two elements is $n^2/2$. Then we can calculate the contact number by integration of the product of these three factors

$$f = \iiint p^2vn^2/2 \; dxdydz$$

and we get

$$f = vn^2\sigma^{-3}/16\pi^{1\cdot5} \tag{6}$$

The total excess energy U must be

$$U = fu = vun^2\sigma^{-3}/16\pi^{1\cdot5} \tag{7}$$

If there are various degrees of contact, and the values of energy are u_1 in the range v_1, u_2 in the range v_2, etc., then U must be

$$U = (v_1u_1 + v_2u_2 + \ldots.)n^2\sigma^{-3}/16\pi^{1\cdot5} \tag{7a}$$

The equation (7) includes the eq. (7a), if we consider that

$$vu = v_1u_1 + v_2u_2 + \ldots.$$

4. The corrected mean of σ .... approximation.

The distribution of σ must be corrected by the factor

$$\exp(-U/kT) \tag{8}$$

But in the case where the change of this factor is not so large in the frequent range of σ, we can take only the first term of the expansion at the neighbourhood of $\sigma = \sigma_0$. Then we have

$$\langle\sigma^2\rangle = b^2a^2n/18 + \sqrt{3}\,vun^{1\cdot5}/4\pi bakT \tag{9}$$

$$\langle\sigma^3\rangle = 4b^3a^3n^{1\cdot5}/81\sqrt{3} + (15\pi - 32)\,vun^2/64\pi^{2\cdot5}kT \tag{10}$$

The equation (9) giving the mean square of radius of gyration has the correction term proportional to $n^{1\cdot5}$. This term is positive, when u is positive or in other words the solvation makes the energy low and the force between the parts of chain is repulsive. In the contrary this term is negative, when u is negative or in other words the solvation does not lower the energy and force is attractive. The behaviour of the second term of the equation (10) is quite similar.

It must be noticed that the ratio of the second term to the first term is proportional to $n^{0\cdot5}$ and becomes larger with the increasing value of n. For it has been expected that the ratio of corrections of this kind tends to zero in the limiting case $n \to \infty$.

5. Specific viscosity....approximation.

If specific viscosity η_{sp} is given by Debye's formula

$$\eta_{sp}/c \propto \langle\sigma^2\rangle \tag{11}$$

where c is the weight concentration of the solution, eq. (9) leads to

$$\eta_{sp}/c = C_1 n + C_2 n^{1\cdot5} \tag{12}$$

in which C_1 and C_2 are constants and their ratio must be

$$C_2/C_1 = 9\sqrt{3}\,vu/2\pi^2 b^3 a^3 kT = 0.788 vu/b^3 a^3 kT \tag{12a}$$

If η_{sp} is given by Einstein's formula

$$\eta_{sp}/c \propto \langle\sigma^3\rangle/n \tag{13}$$

where $\langle\sigma^3\rangle$ is assumed to be proportional to the effective volume, then eq. (10) leads to

$$\eta_{sp}/c = C_1 n^{1\cdot5} + C_2 n^2 \tag{14}$$

in which

$$C_2/C_1 = 81\sqrt{3}\,(15\pi\text{-}32) vu/16^2\pi^2 b^3 a^3 kT = 0.838 vu/b^3 a^3 kT \tag{14a}$$

The value given by (12a) and (14a) contains no arbitrary constant. Now let us try a crude numerical estimation. In paraffine molecule the flexibility constant b^2 is about 6 according to the preceding paper. The contact energy u is assumed to be of the magnitude of the thermal energy kT. And the contact range v is probably about a^3, the volume of the cube with edges of the length of a C-C bond. Then C_2/C_1 in (12a) and (14a) is about 0.005, and the ratio of the second term to the first term in (12) or (14) becomes about $0.05n^{0\cdot5}$. The correction amounts 50% even in the case where n is only 100. This result shows a cause of the failure of the formula of Staudinger's type

$$\eta_{sp}/c = \text{const. } n^{\alpha}, \quad \alpha = 0.5 \sim 1 \tag{15}$$

in applying over the wide range of n (Fig. 5).

This numerical value however seems to be somewhat contradictory to the assumption adopted in the approximation of eq. (8), that the correction is small. We must calculate more accurately.

6. Accurate formulae for repulsion.

Rewriting the factor (8) as

$$U/kT = \beta\sigma^{-3} \tag{16}$$

we calculate the numerical integrations

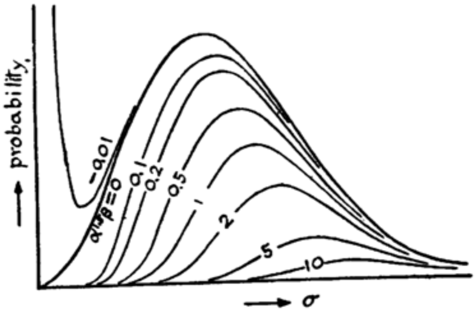

Fig. 3. The effect of intramolecular contacts on the distribution probability of σ.

$$\begin{aligned}\langle\sigma^2\rangle &= \int\sigma^4\exp(-\alpha\sigma^2)\exp(-\beta\sigma^{-3})d\sigma\Big/\int\sigma^2\exp(-\alpha\sigma^2)\exp(-\beta\sigma^{-3})d\sigma\\ &= 1.5\alpha^{-1}(1+f_2)\\ \langle\sigma^3\rangle &= \int\sigma^5\exp(-\alpha\sigma^2)\exp(-\beta\sigma^{-3})d\sigma\Big/\int\sigma^2\exp(-\alpha\sigma^2)\exp(-\beta\sigma^{-3})d\sigma\\ &= 4\pi^{-0.5}\alpha^{-1.5}(1+f_3)\end{aligned}$$

and obtain the numerical values of f_2 and f_3 as the functions of $\alpha^{1.5}\beta$. (Fig. 4). They are proportional to $\alpha^{1.5}\beta$ when they are small, and proportional to the 0.4th and the 0.6 th power of it respectively when they are large. Eqs. (4) and (16) give

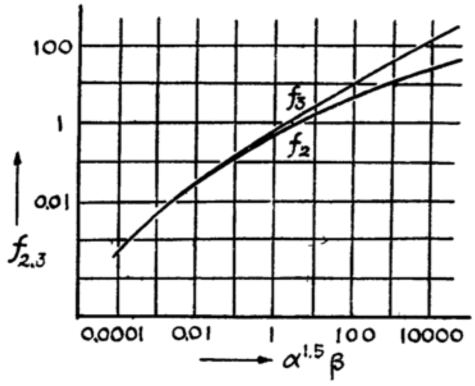

Fig. 4. The correction ratio f_2, f_3.

$$\begin{aligned}\alpha^{1.5}\beta &= (27/b^2a^2n)^{1.5}vun^2/16^{1.5}kT\\ &= 1.575vun^{0.5}/b^3a^3kT\end{aligned}$$

Therefore f_2 and f_3 are proportional to $n^{0.5}$ for small n, and proportional to $n^{0.2}$ and $n^{0.3}$ respectively for large n (Fig. 4).

If the specific viscosity is given by Einstein's formula (13), we have

$$\begin{aligned} \eta_{sp}/c &= \text{const.}\, n^{0\cdot 5}(1+f_3) \\ &\cong C_1 n^{0\cdot 5} + C_2 n^{0\cdot 8}, \text{ for large } n \qquad (17) \end{aligned}$$

where

$$C_2/C_1 = 2.08(vu/b^3a^3kT)^{0\cdot 6}$$

The numerical ratio of the correction term to the first term is about 70% for $n = 100$, and about 300% for $n = 10000$ (Fig. 5).

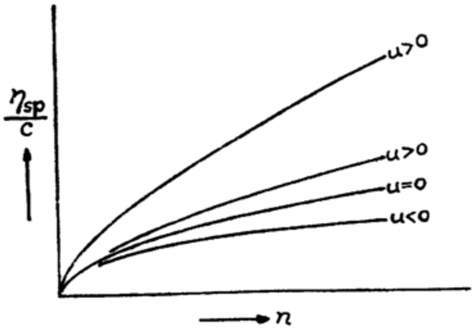

Fig. 5. The relation of viscosity to the molecular weight, and contact energy u.

We can obtain another formula from Debye's (11):

$$\begin{aligned} \eta_{sp}/c &= \text{const.}\, n(1+f_2) \\ &\cong C_1 n + C_2 n^{1\cdot 2}, \text{ for large } n \qquad (18) \end{aligned}$$

7. Self-coagulation by attraction.

If the interaction is attractive and u is negative, β in eq. (16) becomes negative and the factor $\exp(-\beta\sigma^{-3})$ ascends so steeply when σ tends to 0 that the distribution of σ is concentrated at $\sigma = 0$. (Fig. 3). The averages of σ are 0. This means the self-coagulation of a chain molecule owing to its own attractive interaction. So far as the interaction is repulsive the molecule has the configuration of the form of the traces of a Brownian particle or its modification, but when the interaction is attractive the configuration becomes as compact as possible however small be the attraction.

Of course σ can not be just 0, because the smallest σ is that of the closest packed sphere of the molecule. But it may be regarded as 0 for large n in comparison with the loose extended form of the repulsive case. If we can alter the interaction gradually from repulsion to attraction by the change of the temperature or the change of the composition of the solvent, we must find the sudden contraction of the size of the molecule at the moment when the solvation energy turns from positive to negative. It is similar to a phase change.

An example of the self-coagulation into the spherical form in bad solvent is given by the photograph of a polymer molecule by the electron microscope method, where the solvent is the worst one, the air or the vacuum.

If the number of elements n is not so large, the contraction may be gradual. For in this case the size of the closest packed sphere is not negligible so that the concentration of the distribution at $\sigma = 0$ is incomplete. The incompletion is not discussed here. But it is easily proved that we can obtain the approximation formulae (9), (10), (12) and (14) by cutting off the range of the false concentration into the spherical form of the distribution.

Summary.

In order to express the apparent size of a flexible long chain molecule the radius of gyration σ around the centre of mass is an appropriate quantity, and its mean square $\langle\sigma^2\rangle$ has been considered to be proportional to the number of elements of the chain n.

We estimate the effect of the intramolecular interaction and find new equations

$$\langle\sigma^2\rangle = \text{const.}n + \text{const.}n^{1\cdot5}$$

$$\langle\sigma^3\rangle = \text{const.}n^{1\cdot5} + \text{const.}n^2$$

Specific viscosity η_{sp} divided per weight concentration c must be

$$\eta_{\text{sp}}/c = \text{const.}n + \text{const.}n^{1\cdot5}$$

or

$$\eta_{\text{sp}}/c = \text{const.}n^{0\cdot5} + \text{const.}n$$

In these equations the second term can never be neglected for large n. It amounts to one half of the first term even in the case of normal paraffine with only 100 carbon atoms.

For large n the accurate formula

$$\eta_{\text{sp}}/c = \text{const.}n^{0\cdot5} + \text{const.}n^{0\cdot8}$$

is obtained in the case of repulsive interaction, but in respect to the molecule of large molecular weight with attractive interaction the self-coagulation into the very small size is concluded.

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