Method of Calculation of a Shape Parameter for Ovaloid Molecules

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ABSTRACT

The nonsphericity parameter γ related to the Isihara shape
factor for ovaloid polymers f by the relation $f = (\gamma/4) + (1/4)$
is calculated through an expansion of the radius of the mole-
cule in spherical harmonics. The limitations of the method
when applied to polymers with high f are discussed.

The introduction of a shape parameter into the description of some
properties of high polymer solutions, such as the second virial co-
efficient and osmotic pressure, by Isihara and Hayashida [1] has led
Sapse and Wiley [2] to test the validity of the model on simpler mole-
cules such as methane and ethylene.

To do that, they used Gibbons' [3] equation of state for gases with
nonspherical molecules together with the parameter γ defined by
Rigby [4] as

$$\gamma = \overline{R}\,S/V \tag{1}$$

where $\overline{R}$ is the average radius, S is the surface area, and V is the volume of the molecule.

Those values were calculated by using Kihara's [5] method, which is quite cumbersome. Also, the values obtained for γ in the case of CH_4 and C_2H_4 do not correspond exactly to the physical reality, since one would expect ethylene to present a higher degree of nonsphericity than methane. Kihara's volume for methane seems to be smaller than the experimental value obtained, for instance, by viscosity measurements. This lead us to look for a more satisfactory method to calculate γ.

The method consists in using an expression of the molecular radius (considering the molecule as a hard core) as a function of the angle θ, which is the angle made by the radius with the Z axes. The expression used is an expansion in spherical harmonics of the form:

$$R = R_0[1 + x(3\cos^2\theta - 1)] \tag{2}$$

which has been used by Bohr et al. [6] to describe the nonsphericity of atomic nuclei. R_0 is the radius of the nucleus (in our case of the molecule) in spherical form, and x is a shape factor related to the shape factor β used by Bohr by the relation:

$$x = \sqrt{5/16\pi}\ \beta \tag{3}$$

This description corresponds to particles symmetric around the Z axes. Positive x indicates a prolate form while negative x indicates an oblate form.

We calculated R, S, and V in terms of R_0 and x by using the expressions:

$$\overline{R} = \frac{\int_0^{\pi/2} R \sin\theta\ d\theta}{\int_0^{\pi/2} \sin\theta\ d\theta} \tag{4}$$

$$= R_0$$

$$V = 2 \int_0^R \int_0^{\pi/2} \int_0^{2\pi} dv$$

$$= 2(2\pi) \int_0^{\pi/2} \sin\theta \; d\theta \int_0^R r^2 dr$$

$$= \frac{4\pi R_0^3}{3} \; (1 + \frac{12}{5} \; x^2 + \frac{16}{35} \; x^3) \tag{5}$$

The surface area was calculated by using the expressions:

$$Z = R \cos\theta \tag{6}$$

and

$$Y = R \sin\theta \tag{7}$$

Then:

$$S = 4\pi \int_{\pi/2}^0 Y \; \sqrt{(dY/d\theta)^2 + (dZ/d\theta)^2} \; d\theta \tag{8}$$

Since the integral involved a square root we had to use a Taylor series expansion around $x = 0$, so keeping terms only up to and including x^2 we get for S:

$$S = 4\pi \; R_0^2 \; [1 + (16/5) \; x^2] \tag{9}$$

Neglecting terms in x at a power higher than 2 in the volume also (this is a reasonable approximation, since we will show later that x has values around 0.15), we obtain for γ the expression:

$$\gamma = \frac{15 + 48\,x^2}{5 + 12\,x^2} \tag{10}$$

When x = 0, the molecule is spherical and γ takes the value of 3. The parameter β and thus x, is related to the electronic quadrupole moment of the molecule by the relation [6]:

$$\overline{Q} = (3/\sqrt{5\pi})\beta(1 + 0.16\beta) \tag{11}$$

This enables us to express γ in terms of a quantity which is measurable experimentally and which should account well for the non-sphericity of a molecule. To calculate $Q_{electronic}$ we used the expression (12):

$$Q_{exp} = Q_{nuclear} - Q_{electronic} \tag{12}$$

where

$$Q_{nuclear} = \frac{1}{2}\,|e|\,\sum_n Z_n(3z_n^2 - r_n^2) \tag{13}$$

where e is the electronic charge, Z_n is the number of charges of the n nucleus, z_n is the nucleus z coordinate, and r_n is the nucleus distance from the origin. Values for R_0 were taken from viscosity measurements [7, 8].

The experimental values for Q_{exp} were those of Buckingham et al. [9].

$$\overline{Q} = Q_{electronic}/(ZeR_0^2) \tag{14}$$

As shown in Table 1, the values for γ are quite small, but this is to be expected since the molecules listed are not very far away from spheres. To obtain higher values for γ, one would have to look for molecules with higher Q and, accordingly, higher x. Unfortunately, γ is a valuable parameter only for convex bodies, and computer calculations have shown that the maximum value x can take for the molecule to remain convex is 0.143. This fact limits the applicability of the model to molecules with low γ. For ovaloid polymers such as hemoglobin and serum albumin, Isihara finds f (hemoglobin) = 1.27 and f (serum albumin) = 1.6. Since

TABLE 1

Molecule	$\overline{Q}$	x	γ
H_2	0.170	0.065	3.01
N_2	0.265	0.102	3.03
O_2	0.338	0.130	3.04
C_2H_6	0.292	0.112	3.03

$$f = \frac{\gamma}{4} + \frac{1}{4} \tag{15}$$

those numbers lead to the values of γ (hemoglobin) = 4.08 and γ (serum albumin) = 5.4, which imply large values for x, much larger than 0.143. As a matter of fact, for such large values of γ, the method breaks down completely, since the limiting value for x is 1 (x larger than 1 means R < 0).

   In conclusion, the expansion in spherical harmonics of the radius of the molecule can be applied only to molecules quite close to spheres. To be able to apply it to molecules with higher nonsphericity (0.143 < x < 1) one would need to be able to calculate the included volume of concave bodies, which we propose to do next.

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