On Concentration Dependence of Polymer Solution Viscosity

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On Concentration Dependence of Polymer Solution Viscosity†

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In the present article the relation between polymer solution Newtonian viscosity and its concentration is based on the idea that this relation is determined by the macomolecule coil size. This assumption allows, on the one hand, to construct the simple theory of Huggins constant (K_H) and, on the other hand to use viscosimetric data for estimation of the coil size. Therefore the suggested approach seems very productive.

Rather simple assumptions lead to the conclusion that the Newtonian viscosity value is the function of the macromolecule size in the range of moderate concentrations of polymer solutions. The Newtonian viscosity value rises as the concentration of polymer solutions rises and at this the viscosity increase is in proportion to the polymer concentration and is also related and to the rotating friction coefficient. At the same time its value is in proportion to the rotating particle volume and to the environment viscosity if this environment can be supposed as continuous.[1] Thus,

$$d\eta = bv\eta \, dc$$

with η = solution viscosity, c = polymer concentration, v = effective hydrodynamic volume of chain coil, b = coefficient depending from coil form.

Hence it follows

$$\frac{d \ln \eta}{dc} = bv \equiv [\eta]_c \tag{1}$$

Such designation ($[\eta]_c$) is introduced to emphasize the physical meaning of

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this quantity which is analogous to the inherent viscosity for infinitive diluted solution.

Thus it is possible to describe the concentration relation of viscosity if one knows the function

$$[\eta]_c = f(c)$$

The attempts for determining this relation by statistic physics or model methods[3] are unsuccessful because of the insufficient development of the methods. Therefore it is necessary to apply to experimental data.

In articles[4,5] there are results of relations between macromolecule coil sizes and polymer concentration obtained with small angle neutronograthy[4] and paramagnetic label methods.[5] In Figure 1 there is a comparison of numerical integration of obtained curves with data of solution viscosity of corresponding polymers in the first[6] (b) and in the second[7] (a) cases. As can be seen a good correspondence of calculation and experiment is observed in a rather wide concentration interval.

The validity of this approach may be demonstrated in the instance of Huggins constant theory which is for determining the relation between the value K_H and solvent quality expressed by α_0^3 the macromolecule coil swelling coefficient value.

Instead of K_H determined by equation

$$\frac{\eta_{sp}}{c} = [\eta]_0 + K_H[\eta]_0^2 c$$

it is convenient to use the quantity β determined by equation

$$\frac{1}{c}\ln \eta_{\iota} = [\eta]_0 - \beta[\eta]_0^2 c \tag{2}$$

By this

$$\beta = \frac{1}{2} - K_H$$

From Eq. (1):

$$\ln \eta_{\iota} = \int_0^c [\eta]_c \, dc = [\eta]_0 \int_0^c \left(\frac{\alpha_c}{\alpha_0}\right)^3 dc \approx [\eta]_0 c + \frac{3[\eta]_0}{\alpha_0}\left(\frac{d\alpha_c}{dc}\right)_0 \frac{c^2}{2} + \cdots$$

The comparison with Eq. (2) gives:

$$\beta = -\frac{3}{2}\frac{(d\alpha_c/dc)_0}{[\eta]_0 \alpha_0} \tag{3}$$

Thus for determining the relation between viscosity and concentration it is necessary to know the relation between swelling coil coefficient α_c and con-
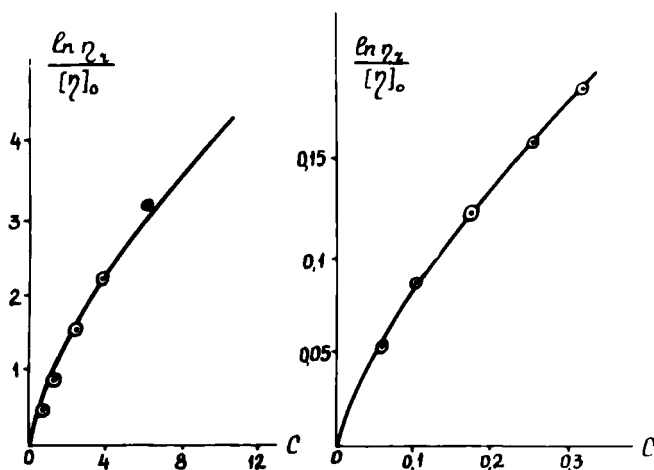
FIGURE 1 Relation between polymer solution viscosity and concentration; curves—integration of Eq. (1); points-experimental data. a—polyvinylbutiral in ethanol; b—polystyrene in dichlorethane.

centration at initial dilution

$$(d\alpha_c/dc)_0$$

There are many attempts to describe at the first approach the exchange of polymer chain dimensions with concentration. The main idea of these theories is that the change of polymer segment concentration leads to the change of solute quality. However for small degrees of swelling all theories show approximately identical results and the comparison of theories with experiment[8] and computer construction of model chains[9] shows that the Flory–Fox equation[10] is the best:

$$\alpha^5 - \alpha^3 = 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)M^{1/2}$$

Insofar as the right side of the equation is in proportion with thermodynamic parameter of excluded volume it is possible to suppose without great error that this quantity is in proportional to polymer concentration.

Assuming that at some critical concentration C_K the swelling coil coefficient has the value of $\alpha_K^3 = \alpha_0^3$. Then the Flory–Fox equation can be represented as following:

$$\alpha^5 - \alpha^3 = \alpha_0^5 - \alpha_0^3 + \frac{C}{C_K}(\alpha_K^5 - \alpha_K^3 - \alpha_0^5 + \alpha_0^3) \tag{4}$$

with respect to Eq. (3)

$$\beta = -\frac{3}{2}\left(\frac{\alpha_K}{\alpha_0}\right)^3 \frac{\alpha_K^5 - \alpha_K^3 - \alpha_0^5 + \alpha_0^3}{\alpha_0^3(5\alpha_0^2 - 3)} \cdot \frac{!}{[\eta]_K C_K} \tag{5}$$

It is convenient to analyse equation (5) in the form:

$$\alpha_0^6(5\alpha_0^2 - 3) = -\frac{3}{2}[\alpha_K^5 - \alpha_K^3 - \alpha_0^5 + \alpha_0^3]\frac{\alpha_K^3}{A} \qquad (6)$$

where $A = [\eta]_K C_K$ is a constant quantity for a given system, a volume filling measure.

Thus it is necessary to investigate the dependence of

$$\mathscr{Y}_1 = \alpha_0^6(5\alpha_0^2 - 3)\beta$$

on

$$\mathscr{Y}_2 = \alpha_0^5 - \alpha_0^3$$

Figure 2 gives the data for some polymers: polystyrene,[8, 11-14] polymethyl-
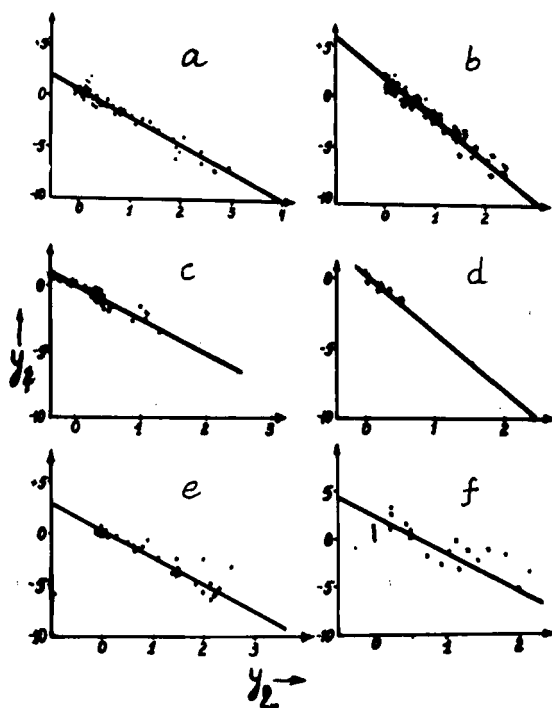
FIGURE 2   Huggins constant relation to coil swelling degree in the coordinates of eq. (6).
a—polystyrene; b—polymethylmethacrylate; c—polyvinylacetate; d—polyisoprene; e—poly-
isobutylene; f—poly-2-hydroxyethylmethacrylate.

methacrylate,[15-17] polyvinylchloride,[18] polyisobutylene,[16, 20-21] polyiso-
prene,[16] poly-4-vinylpyridene,[21] polyvinylacetate,[22] poly-2-hydroxyethyl-
methacrylate.[23] Evidently, Eq. (6) describes experimental data satis-
factorily and at this the correlation coefficient $\imath$ has high value (Table I).

TABLE I
Equation (6) for some polymers

Polymer	A	α_K^3	$-\imath$	N
Polyisobutylene	0.65 ± 0.57	1.06 ± 0.64	0.94	44
Polyvinylchloride	0.61 ± 0.57	1.46 ± 0.73	0.95	42
Polymethylmethacrylate	0.59 ± 0.29	1.45 ± 0.40	0.78	73
Polyisoprene	0.40 ± 0.78	1.08 ± 0.55	0.99	8
Polyvinylacetate	0.60 ± 0.55	0.95 ± 0.58	0.96	45
Poly-2-hydroxyethyl-methacrylate	0.67 ± 0.37	1.46 ± 0.58	0.91	25
Polystyrene	0.67 ± 0.29	1.26 ± 0.38	0.97	67

It is to be noted the curve for polystyrene with values of and A taken from the Table I describes experimental data better than the Peterson–Fixman theoretical curve[24] (Figure 3, curve 2).

The value of α_K^3 changes from 1 (polyvinylacetate) to 1.5 (polymethyl-methacrylate and polyvinylchloride); yet it is rather difficult to find the dependence between α_K^3 and polymer chain properties. In any case it is obvious that the coil sizes are far off θ-dimensions at critical concentration as follows from theoretical[25] and experimental[4] data.

The value of A is almost constant (0.65) for all systems. If the concentration dependence of viscosity is described with the Einstein equation (incompressible hard balls) then $A = 2.5$. For macromolecular coils taking into account the Flory–Fox formula[26]

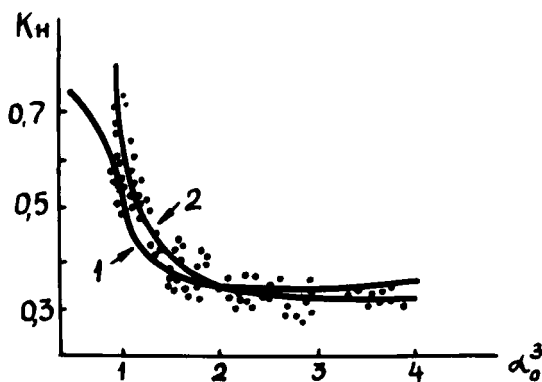$$[\eta] = \Phi \frac{\langle \imath^2 \rangle^{3/2}}{M}$$

$A = 1.3 \div 1.4.$

FIGURE 3   Relation between K_H and α_0^3; point—experimental data: 1—calculated curve from Peterson–Fixman theory; 2—calculated curve from eq. (5).

Apparently twice as small a value of A means the polymer coil constant is securing identical thermodynamic conditions inside and outside the coil.

Thus the assumption that the derivative of the logarithm of viscosity with concentration is a measure of the hydrodynamic volume and successfully relates to the Huggins constant. Therefore the assumption is quite reasonable. Thus simple viscosity measurements as a function of concentration allows the estimation of coil size in that concentration range where polymer solution flow is not complicated by strong interchain interaction.

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