

# polymer communications

## A new approach to calculating the molecular draining effect from sedimentation and diffusional data\*

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Treatment of experimental dependence of the translational friction coefficient on molecular weight,  $f(M)$ , obtained for semi-flexible macromolecules, is discussed. A draining effect is significant for these chains and must be taken into account to determine the correct values of unperturbed dimensions of the macromolecule. For this purpose a new relation between the Flory factor  $P$  and the scaling exponent  $b$  (in the equation  $f = K_f M^b$ ) has been proposed. According to the Yamakawa theory developed for translational friction of the wormlike chains, the relation is valid for macromolecules with any length exceeding two times the statistical segment length, and with any diameter. The method has been applied to hydrodynamic properties of poly(chlorohexyl isocyanate) in carbon tetrachloride. Copyright © 1996 Elsevier Science Ltd.

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### Introduction and definitions

Permeability of the macromolecule to the solvent (effect of the partial draining of solvent) influences significantly the hydrodynamic properties of a polymer. Recently we discussed the influence of the effect on molecular-weight dependence of these properties<sup>1</sup>, noticeable particularly for rigid and semi-flexible polymers. In the present study, a new possibility to take the effect into account in determination of unperturbed dimensions of the macromolecule is presented.

The sedimentation coefficient ( $s$ ) and the translational diffusion coefficient ( $D$ ) are both quantities well-known as being sensitive to the dimensions of the macromolecule and the partial draining of the solvent. Therefore, sedimentation and diffusional data are often used, like data of viscometry, for determination of such conformational parameters of the macromolecule as the statistical segment length (Kuhn segment length,  $A$ ), mass per chain length unit ( $M_L$ ) and the chain diameter ( $d$ ). The  $s$  and  $D$  values extrapolated to zero concentration are related to translational friction coefficient ( $f$ ) of the macromolecule in solution by

$$f = M(1 - \bar{v}\rho)/s_0 N_A \quad (1)$$

$$f = kT/D_0 \quad (2)$$

where  $M$  is molecular weight,  $N_A$  is the Avogadro number,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\bar{v}$  is a partial specific volume of the solute, and  $\rho$  is the solvent density.

*Conformational parameters.* Coefficient  $f$  may be related to the end-to-end distance ( $h$ ) in the macromolecule by

$$f/\eta_s = P(\langle h^2 \rangle_0)^{1/2} \alpha \quad (3)$$

where  $\eta_s$  is the solvent viscosity,  $\alpha$  is the expansion coefficient,  $\alpha = (\langle h^2 \rangle / \langle h^2 \rangle_\theta)^{1/2}$ ,  $\langle h^2 \rangle_\theta$  and  $\langle h^2 \rangle$  are the mean-square values of  $h$  in  $\theta$  and non- $\theta$  solvent, respectively, and  $P$  is a hydrodynamic factor.  $P$  is decreasing with increasing excluded volume effects,  $P = P(\alpha)$ , and, for the impermeable polymer coil in  $\theta$  solvent ( $\alpha = 1$ ), it is equal to  $P_\theta = \lim(T \rightarrow \theta) P = 5.11^2$ .

On the other hand, in random coil limit ( $M \rightarrow \infty$ ), we can write

$$\langle h^2 \rangle_\theta = AL = AM/M_L \quad (4)$$

Thus, conformation parameters of the macromolecule are related to  $s_0$  and  $D$  by

$$A = (kT/P_\theta \eta_s)^2 M_L / (D^2 M) \quad (5)$$

$$A = (P_\theta N_A)^{-2} M_L M / [s]^2 \quad (6)$$

Here  $[s] \equiv s_0 \eta_s / 1 - \bar{v}\rho$ .

*Unperturbed dimensions of the isolated macromolecule.* In non- $\theta$  solvent, the influence of volume effects on macromolecule dimensions is usually excluded by extrapolation of the hydrodynamic data to the range of negligible volume effects ( $M \rightarrow 0$ ) in coordinates  $1/DM^{1/2}$  (or  $M^{1/2}/[s]$ ) versus  $M^{1/2}$ <sup>3</sup>. Then  $A$  is evaluated from the intercept by means of equation (5) or equation (6).

*Draining effect.* When excluded volume effects are negligible, the draining of solvent may be taken into account by extrapolation of the data to infinite molecular weight (the non-draining limit) by plotting  $DM$  or  $[s]$  versus  $M^{1/2}$ . According to theory<sup>4</sup>, the length  $A$  is calculated from the slope of the dependence in the range of  $L/A \geq 2.27$  by means of equation (7) or

\* Dedicated to Professor Walther Burchard on his 65th birthday

equation (8):

$$DM = kT(\eta_s P_\infty)^{-1} (M_L/A)^{1/2} M^{1/2} + kTM_L(3\pi\eta_s)^{-1} [\ln(A/d) - \gamma] \quad (7)$$

$$[s] = (N_A P_\infty)^{-1} (M_L/A)^{1/2} M^{1/2} + M_L(3\pi N_A)^{-1} [\ln(A/d) - \gamma] \quad (8)$$

where  $\gamma = 1.056^2$ .

In other words, the  $P$  parameter is taken here to be equal to  $P_\infty = \lim(L/A \rightarrow \infty)P$ , and the draining effect is related to the inapplicability of equation (4) with  $P = P_\theta$ , and, hence, equations (5) and (6), to treatment of the permeable macromolecule properties.

*Dependence of  $P$  on the chain length and diameter.* Yamakawa and co-workers<sup>2</sup> accepted that equation (4) is valid at any  $L/A$  value, and referred the draining effect to dependence of  $P$  on a draining parameter  $L/A$  and  $d/A$ . They have evaluated  $P$ , tabulating the function  $\Gamma_2 = 3 \log(P_\infty/P)$  versus  $\log(L/A)$  at different  $d/A$  for the wormlike cylinder model<sup>2</sup>. Later, these calculations were specified for short chains by using the wormlike sphere-cylinder model<sup>5,6</sup>. Figure 1 shows that for this model, the  $P$  factor strongly depends on  $L/A$  and  $d/A$  in a complicated manner.

These  $P(L, d)$  dependences were confirmed practically by the results of Kamide and Saito<sup>7</sup>. They have attempted to describe the function  $P(L, d)$  by the semi-empirical relation  $P = K_p M^{\alpha_p}$ . They collected  $K_p$  and  $\alpha_p$  values obtained from the experimental data available for a number of cellulose derivatives<sup>8</sup>. In accordance with theoretical predictions (Figure 1), these quantities,  $K_p$  and  $\alpha_p$ , are different for different polymers which can be assumed to have a different chain cross-section.

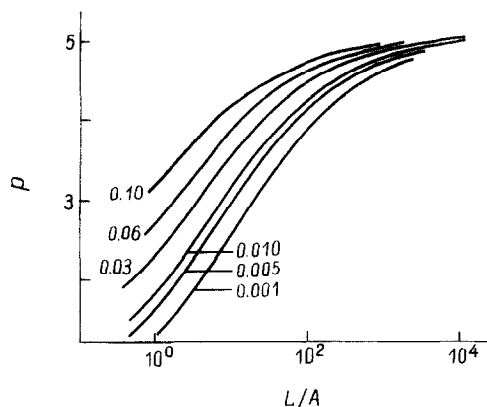
### Results and discussion

*New approach.* We accept below the wormlike sphere-cylinder model, with length ( $L$ ), diameter ( $d$ ), shift factor ( $M_L$ ) and persistent length ( $A/2$ ). We assume also that the excluded volume effects are absent. The  $P$  factor for this model is shown in Figure 1. Earlier, for the same model, we have evaluated<sup>1</sup> the scaling exponent  $b$  in equation

$$D = K_D M^{-b} \quad (9)$$

It was shown that, like the  $P$  factor, the  $b$  exponent strongly depends on the  $L/A$  and  $d/A$  values.

A surprising observation is apparent if we juxtapose



**Figure 1**  $P$  plotted against  $L/A$  for wormlike sphere-cylinder model chains with the indicated  $d/A$  values evaluated according to references 5 and 6 with  $P_\infty = 5.11$

the  $P$  and  $b$  values obtained at the same  $L/A$  and  $d/A$  values. Some of the principal ones are listed in Table 1 and, in more detail, in Figure 2.

In the range of  $L/A \geq 2$ , the  $P$  factor depends linearly on the  $b$ . Moreover, the linear parts of different partial dependences form a common straight line which can be reliably described as

$$P/P_\infty = 1 - 2.006(b - 0.5) \quad (10)$$

This means that the  $b$  exponent may be used as a quantity of the draining effect to choose a suitable  $P$  value. Then, conformation parameters may be evaluated by using equation (5) or (6). We should mention once again that this treatment can be employed only when  $L/A \geq 2$ , i.e. it is inapplicable for very short macromolecules.

*Consistent order in calculations.* Application of the method consists of the following steps: (a) an  $M$  range is chosen where  $s_0$  or  $D$  depends linearly on  $M$  in log-log coordinates; (b) the  $b$  exponent value in equation (9) is determined from the slope; (c) substituting the  $b$  value into equation (10) we have  $P$ ; (d) by means of equation (5) or (6),  $A$  is evaluated from the average value of  $M/s_0^2$  or  $MD^2$ ; (e) validity of the method is checked by satisfaction of the requirement  $L/A \geq 2$ , or the new  $M$  range is treated.

*Comparison with experimental data.* The method has been applied to hydrodynamic properties of

**Table 1** The  $b$  exponent and the ratio  $P/P_\infty$  for the wormlike sphere-cylinder model chains with the different  $d/A$  values evaluated according to references 5 and 6 with  $P_\infty = 5.11$

$d/A = 0.10$							
$b$	0.568	0.623	0.653	0.611	0.587	0.532	0.503
$P/P_\infty$	0.589	0.628	0.696	0.770	0.825	0.938	0.994
$d/A = 0.06$							
$b$	0.624	0.669	0.691	0.644	0.615	0.544	0.505
$P/P_\infty$	0.488	0.539	0.614	0.702	0.768	0.914	0.911
$d/A = 0.010$							
$b$	0.757	0.775	0.779	0.727	0.688	0.581	0.509
$P/P_\infty$	0.296	0.356	0.433	0.538	0.621	0.839	0.982
$d/A = 0.005$							
$b$	0.788	0.801	0.802	0.749	0.710	0.594	0.511
$P/P_\infty$	0.257	0.314	0.389	0.493	0.579	0.813	0.978

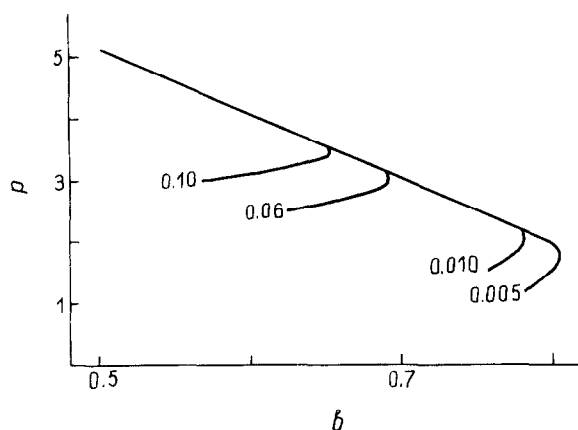


Figure 2  $P$  plotted against  $b$  for wormlike sphere-cylinder model chains with the indicated  $d/A$  values evaluated according to references 5 and 6

poly(chlorohexyl isocyanate) in carbon tetrachloride<sup>9</sup>. Dependence of  $D$  on  $M$  for eight fractions with high molecular weight,  $M \geq 70 \times 10^3$ , could be reliably approximated by equation (9) with the only numerical value of  $b$ , equal to  $(0.68 \pm 0.03)$  and  $K_D = 4.89 \times 10^{-4}$  with  $r = 0.995$  ( $r$  being the linear regression coefficient for the log-log plotting). Substituting  $b = 0.68$  into equation (10), we obtain  $P = 3.265$ .

For this polymer,  $\eta_s/1 - \bar{\nu}\rho = -3.64 \times 10^{-2} \text{ g cm}^{-1} \text{ s}^{-1}$  and  $M_L = 77 \times 10^8 \text{ cm}^{-1}$ <sup>9</sup>. The average value of  $M/s_0^2$  for the fractions selected was  $(2.54 \pm 0.47) \times 10^{30}$ . Substituting these values with  $P = 3.265$  into equation (6), we obtain  $A = 380 \pm 70 \text{ \AA}$ . This coincides with the  $A_f = 420 \pm 50 \text{ \AA}$  value obtained by Vitovskaya *et al.*<sup>9</sup> from the sedimentation data treated by Hearst-Stockmayer plotting<sup>4</sup>. This confirms the reliability of the proposed method when applied to the draining effect calculation to achieve characterization of equilibrium rigidity of the macromolecule.

Applicability of the method to the data used can be checked as follows. When  $A = 380 \text{ \AA}$  and  $M_L = 77 \text{ \AA}^{-1}$ , the condition that  $L/A \geq 2$  is equivalent to  $M \geq 2AM_L = 60 \times 10^3$ . We see that the condition is satisfied for the fractions used, and, hence, the method is applicable.

#### Concluding remarks

The method is intended for treatment of sedimentation or diffusional data obtained for semi-flexible macromolecules with noticeable draining effect, when the excluded volume effects may be ignored. The method is based on the universal dependence of  $P$  on  $b$  which may be described (as follows from analysis of the theory<sup>5,6</sup>) as linear expression (10) with numerical coefficients independent of the  $d$  value (at  $L/A \geq 2$ ). As it turns out, such universal treatment is more easily achievable for the translational friction data than the viscometry data.

Actually, an earlier attempt was undertaken<sup>10</sup> to find a correlation between the Flory factor  $\Phi$  defined by  $\Phi = [\eta]M/(\langle h^2 \rangle)^{3/2}$  and the  $\alpha$  exponent in the Mark-Kuhn-Houwink-Sakurada equation  $[\eta] = K_\eta M^\alpha$  (here  $[\eta]$  is intrinsic viscosity). Treatment of the experimental data available for the number of semi-flexible polymers has resulted in the empirical relation<sup>10</sup>

$$\Phi = 0.52 \times 10^{23} \alpha^{-2.32} \quad (11)$$

It was assumed by Dondos and Staikos<sup>10</sup> that relation (11) is universal and suitable for elimination of the draining effect on unperturbed dimensions of the macromolecule.

A more complicated dependence of  $\Phi$  on  $\alpha$  is, however, predicted by the theory of intrinsic viscosity developed for the wormlike chains<sup>11,12</sup>. The dependence may be well approximated by expressions (12) and (13) for thin and thick chains, respectively<sup>13</sup>

$$\log(\Phi/\Phi_\infty) = -0.645\alpha \quad (d/A = 0.005; L/A \geq 2) \quad (12)$$

$$\log(\Phi/\Phi_\infty) = -0.517\alpha \quad (d/A = 0.10; L/A \geq 5) \quad (13)$$

Dependence  $\Phi(\alpha)$  is obviously different for chains with different cross-sections (the difference in  $\Phi$  reaches 25% for the diameter values shown). On the other hand, the  $\Phi$  value predicted by the theory differs significantly from the  $\Phi$  value which follows from the experimental data (equation (11)).

Finally, the other limiting values,  $\Phi_\infty = 2.36 \times 10^{23} \text{ mol}^{-1}$  and  $P_\infty = 6.20$  recently obtained<sup>14,15</sup> may be used in the calculations.

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#### References

- 1 Lavrenko, P. N. *Polymer* 1990, **31**, 1481
- 2 Yamakawa, H. and Fujii, M. *Macromolecules* 1973, **6**, 407
- 3 Cowie, J. M. G. and Bywater, S. *Polymer* 1965, **6**, 197
- 4 Hearst, J. E. and Stockmayer, W. H. *J. Chem. Phys.* 1962, **37**, 1425
- 5 Norisuye, T., Motovoka, M. and Fujita, H. *Macromolecules* 1979, **12**, 320
- 6 Yamakawa, H. and Yoshizaki, T. *Macromolecules* 1979, **12**, 32
- 7 Kamide, K. and Saito, M. *Eur. Polym. J.* 1982, **18**, 661
- 8 Kamide, K. and Miyazaki, Y. *Polym. J.* 1978, **10**, 539
- 9 Vitovskaya, M. G., Lavrenko, P. N., Shtennikova, I. N., Gorbunov, A. A., Peter, T. V., Korneeva, E. V., Astapenko, E. P., Getmanchuk, Yu. P. and Tsvetkov, V. N. *Vysokomol. Soedin. (A)* 1975, **17**, 1917
- 10 Dondos, A. and Staikos, G. *Colloid Polym. Sci.* 1995, **273**, 626
- 11 Yamakawa, H. and Fujii, M. *Macromolecules* 1974, **7**, 128
- 12 Yamakawa, H. and Yoshizaki, T. *Macromolecules* 1980, **13**, 633
- 13 Lavrenko, P. N. *Colloid Polym. Sci.* in press
- 14 Oono, Y. *Adv. Chem. Phys.* 1985, **61**, 301
- 15 Oono, Y. and Kohmoto, M. *J. Chem. Phys.* 1983, **78**, 520