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Treating any polymer dissolved in water as polymer presenting a draining effect

Anastasios Dondos

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Abstract The statistical segment length of a large number of flexible and rigid polymers dissolved in water is calculated. For these calculations, the constant value of the Flory's parameter Φ ($\Phi = 2.6 \times 10^{23}$ cgs) along with its values obtained from an equation proposed for polymers exhibiting a significant draining effect (Colloid Polym Sci 273: 626–632, 1995) are used. Applying the first approximation for Φ, a very low statistical segment length for the polymers dissolved in water is obtained, while in the second case the statistical segment length is almost identical with the values obtained when these polymers are dissolved in an organic solvent. Moreover, we show that there is an optional application of the modified universal calibration of the gel permeation chromatography (J Polym Sci B Polym Phys 41: 707–710, 2003), only if we use values of Φ obtained via the second approximation for polymers presenting a significant draining effect (Colloid Polym Sci 273: 626–632, 1995).

Keywords Hydrosoluble flexible polymers · Draining effect · Flory's parameter Φ · Molecular dimensions · Modified universal calibration

Introduction

It is generally considered that a constant value of the Flory parameter Φ can be applied if all of the solvent in the polymer coil is essentially trapped and unable to move in and out of the coil in a time comparable with the relaxation time of the polymer coil. Nevertheless in many cases solvent molecules near the periphery of the coil are quite free to move independently of the coil. If this phenomenon takes place, we consider that the coil presents a draining effect and the value of the

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A. Dondos (✉)
Department of Chemical Engineering, University of Patras, 26504 Patras, Greece
e-mail: dondos@chemeng.upatras.gr

parameter Φ decreases. When the coil presents a stiffness (wormlike polymer) and it is dissolved in any solvent (water or organic solvent), this phenomenon is aggravated and the parameter Φ takes very low values [1].

In the case of flexible polymers dissolved in organic solvents (contrary of the wormlike polymers) using the constant value of Φ obtained in theta conditions (2.5×10^{23} or 2.6×10^{23} cgs) we obtain from viscosity data correct values for their dimensions. Nevertheless, we have observed that even flexible polymers must present a draining effect when they are dissolved in water, because only if we take into account values of Φ lower than 2.5×10^{23} we obtain correct values for their dimensions [2–4]. For these values of Φ, for the flexible polymers dissolved in water, we use an empirical equation relating the value of Φ with the quality of the solvent [5] as this quality is expressed by the exponent a of the Mark–Houwink–Sakurada (MHS) equation. This equation has been originally proposed for the wormlike polymers.

In this article, we shall show that with values of Φ obtained from the proposed equation [5], we obtain correct values for the statistical segment length of any flexible polymer dissolved in water, or in solvent mixtures containing water, while with the constant value of Φ (2.6×10^{23}), we obtain erroneous values for the statistical segment length of these polymers.

We will also show, in this article, that using the value of Φ obtained from the proposed equation [5], we have a good applicability of the modified universal calibration of the gel permeation chromatography (GPC) [6] when the solvent is water.

Theoretical and procedure

Based on the results obtained by Yamakawa and Fujii [1], concerning the Flory's parameter Φ of the wormlike polymers we have proposed the following equation [5] relating the value of this parameter with the quality of the solvent in which each polymer is dissolved

$$\Phi = 0.52 \times 10^{23} a^{-2.32} \tag{1}$$

In this relation, a is the exponent of the MHS equation expressing the quality of the solvent. The above equation is theoretically justified [7, 8], and it is used to obtain the Φ value of many wormlike polymers dissolved in different solvents (organic solvents or water) [9, 10] and many flexible polymers dissolved in water [2–4]. Equation 1 was also used for the study of polyelectrolytes [11, 12] considering that these polymers also behave as polymers with a draining effect.

The Kuhn statistical segment length, A, of the polymers is often obtained from the well-known equation,

$$A = \left(\frac{K_\theta}{\Phi}\right)^{2/3} M_\mathrm{L} \tag{2}$$

in which K_θ is the viscometric unperturbed dimensions parameter ($K_\theta = [\eta]_\Theta / M^{1/2}$) and M_L the molecular mass per contour length. Only using a value of Φ obtained from Eq. 1, we will obtain correct values for the statistical segment length for the flexible polymers dissolved in water as we have already mentioned.

The viscometric unperturbed dimensions parameter, K_θ, will be obtained from graphical methods based on the Stokmayer–Fixman–Burchard (SFB) equation [13, 14]

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi B M^{1/2} \tag{3}$$

or in the Dondos–Benoit (DB) equation [15]

$$1/[\eta] = -A_2 + K_\theta^{-1}/M^{1/2}. \tag{4}$$

In the above equation, $[\eta]$ is the intrinsic viscosity of each polymer fraction. Plotting $[\eta]/M^{1/2}$ versus $M^{1/2}$ according to the SFB equation, we obtain a straight line the extrapolating of which in M equal to zero we give the value of K_θ. In the case of DB equation, the slope of the obtained straight line, plotting $1/[\eta]$ versus $1/M^{1/2}$, we give the inverse of K_θ.

In the "classical" universal calibration of the GPC [16], the hydrodynamic volume of the macromolecule is expressed by the product $[\eta]M$, according to the well-known Fox–Flory equation,

$$[\eta] = \frac{\Phi (R^2)^{3/2}}{M} \tag{5}$$

and considering the Φ value as a constant. In the above equation, R is the radius of gyration of the macromolecule, and R^3 expresses its hydrodynamic volume.

In the case of polymers presenting a draining effect (flexible polymers dissolved in water and wormlike polymers dissolved in any solvent) it is evident that we must take into account not a constant value for Φ, as we have already mentioned, but a value obtained from Eq. 1 and express the hydrodynamic volume by $[\eta]M/\Phi$.

Results and discussion

The experimental results are taken from the literature and are treated according to the previous equations.

Poly(ethylene oxide) (PEO)

PEO is one of the most studied hydrosoluble polymers. Many studied concern its molecular dimensions in solution in pure water, in water containing different salts, and in organic solvents. The molecular dimensions of PEO expressed by the Kuhn statistical segment length, A, have often been obtained using different graphical methods.

In Fig. 1, we present the application of Eq. 3 with fractions of PEO dissolved in three different solvents. When benzene is the solvent [17], we obtain $K_\theta = 22.2 \times 10^{-2}\ \mathrm{cm^3\ gr^{-3/2}\ mol^{-1/2}}$ (curve A), in pure water [18] we obtain $K_\theta = 6.10^{-2}$ (curve B), and in 0.1 M aqueous sodium chloride solution [19] we obtain

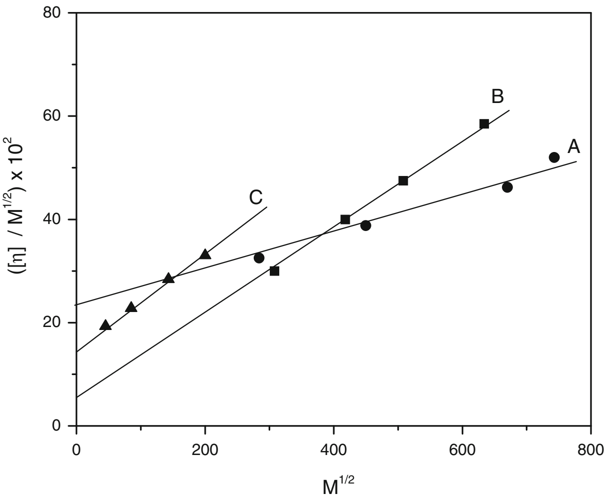

Fig. 1 SFB plots for PEO: in benzene, curve *A*; in pure water, curve *B*; and in 0.1 M aqueous sodium chloride solution, curve *C*

$K_\theta = 14.5 \times 10^{-2}$ (curve C). Using the "constant" value of Φ ($\Phi = 2.6 \times 10^{23}$ cgs) and applying Eq. 2, with $M_L = 34$ gr mol^{-1} Å^{-1}, we must obtain from the values of K_θ, three different values for the Kuhn statistical segment length *A* of PEO.

Accepting now that in water and in 0.1 M aqueous NaCl solution, the PEO presents a draining effect, and obtaining the values of Φ from Eq. 1 (Table 1), we obtain for *A* the same values in these two solvents from Eq. 2 (12 and 11 Å, Table 1). The same value we obtain in benzene accepting that PEO, as a flexible polymer, does not present a draining effect in this organic solvent and consequently we use the value for $\Phi = 2.6 \times 10^{23}$ (Table 1). If we accept that in water and in 0.1 aqueous NaCl solution, the PEO does not present a draining effect as in benzene, and using 2.6×10^{23} for the value of Φ, the obtained values for *A* are very low (Table 1). Especially in pure water, the value of *A* ($A = 6$ Å) is the half of the value obtained in benzene although water is a better solvent for PEO than benzene.

Woodley et al. [20] have also proposed the existence of draining effect for PEO when this polymer is dissolved in water.

Polyacrylamide (PAAm)

The PAAm is mainly studied in pure water and in salt aqueous solution in a very large molecular mass region [21, 22]. The draining effect of this polymer has been studied here using the results obtained in the study of Duval et al. [22] because in this study except the study of the molecular dimensions of PAAm, we found the behavior of this polymer in the gel permeation chromatography.

The proposed by Benoît et al. [16] universal calibration of GPC (log$[\eta]M$ versus elution volume) has applied with fractions of PAAm dissolved in 0.1 N NaCl

Table 1 The MHS exponent *a*, the unperturbed dimensions parameter K_θ, the Flory's parameter Φ, and the Kuhn statistical segment length *A*, obtained for six polymers dissolved in organic solvents, water, and mixtures containing water

Polymer	Solvent	a	$K_\theta \times 10^2$	$\Phi \times 10^{-23}$ cgs	A (Å)
PEO	H_2O	0.79	6.0	2.6	6
PEO	H_2O	0.79	6.0	0.9	12
PEO	0.1 NaCl	0.68	14.0	2.6	8
PEO	0.1 NaCl	0.68	14.0	1.5	11
PEO	Benzene	0.73	22.2	2.6	12
PAAm	0.1 NaCl	0.65	8.2	2.6	13
PAAm	0.1 NaCl	0.65	8.2	1.4	20
Polycaprolactam	*m*-cresol	0.745	40.5	2.6	17
Polycaprolactam	PTF–H_2O	0.76	17.0	2.6	9
Polycaprolactam	PTF–H_2O	0.76	17.0	0.99	18.5
P4VP	Abs-Eth.	0.68	9.25	2.6	21
P4VP	But–isop.	0.57	8.6	2.6	20
P4VP	Eth–H_2O	0.73	3.55	2.6	11
P4VP	Eth–H_2O	0.73	3.55	1.08	20
Denaturated protein	H_2O	0.69	9.7	2.6	12
Denaturated protein	H_2O	0.69	9.7	1.23	24
DNA	H_2O	0.73	166.0	2.6	650
DNA	H_2O	0.73	166.0	1.08	1200

aqueous solution and was compared with the results obtained with fractions of PEO dissolved in water [22]. As we can see in Fig. 2a, in the high molecular mass region ($M > 100.000$) the points are found in the same curve as it is predicted by Benoît et al. method. In the contrary, in the low molecular weight region ($M < 100.000$) the points are found in two distinct curves.

In the modified universal calibration [6] ($\log([\eta]M/\Phi)$ versus elution volume) we must use, for PAAm, two different values for Φ ($\Phi = 1.41 \times 10^{23}$ for the low molecular mass region and $\Phi = 1.01 \times 10^{23}$ for the high molecular mass region). This is due to the fact that the PAAm presents in 0.1 N NaCl aqueous solution two different exponent in the MHS representation [22] ($a = 0.65$ in the low molecular mass region and $a = 0.75$ in high molecular mass region). The above mentioned two values of Φ have been obtained from Eq. 1 using these two values of a. For PEO in water we have the same value for the MHS exponent in the entire molecular mass region ($a = 0.77$) and from Eq. 1 we obtain $\Phi = 0.9 \times 10^{23}$ which lies very close to the Φ value obtained for PAAm in the high molecular mass region ($\Phi = 1.01 \times 10^{23}$).

Applying now the modified universal calibration, as we can see in Fig. 2b, we obtain a single curve with the fractions of PAAm and PEO in the entire molecular mass region. This result indicates that the PAAm, as the PEO, must present a draining effect and that the modified universal calibration of GPC presents a general applicability, if the adequate values of Φ are used, as obtained from Eq. 1.

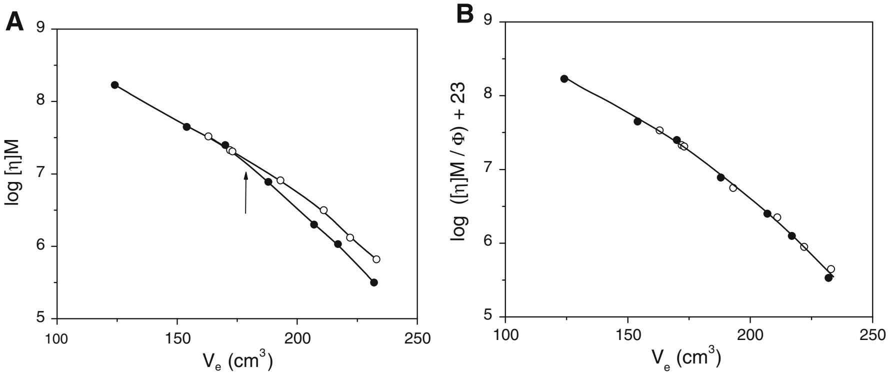

Fig. 2 Universal calibration of GPC for PEO (*filled circle*) and PAAm (*unfilled circle*). **a** According to the "classical" universal calibration and **b** according to the modified universal calibration

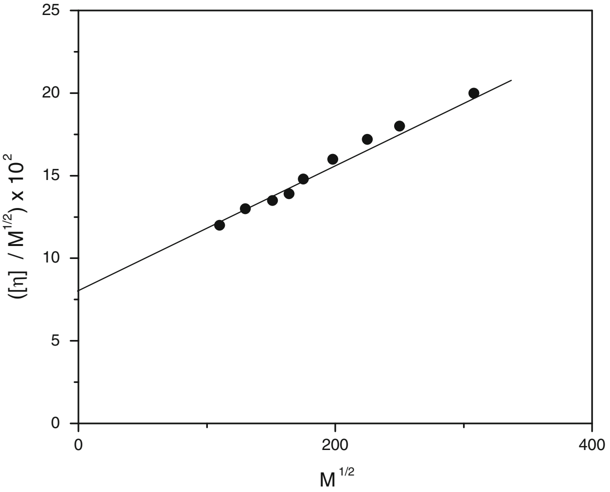

Fig. 3 SFB plot for PAAm in 0.1 N NaCl aqueous solution

With the viscometric results obtained with the fractions of PAAm in the low molecular mass region [22] and applying the SFB equation (Eq. 3), we obtain $K_\theta = 8.2 \times 10^{-2}$ cm^3 gr^{-1} (Fig. 3). A comparable value for K_θ (7.9×10^{-2}) has been proposed by Kulicke et al. [21], when PAAm is dissolved in water. Considering that the PAAm does not present a draining effect and using for Φ the value of 2.6×10^{23} and with $M_L = 28.4$ gr mol^{-1} Å^{-1} we obtain from Eq. 2 for the statistical segment length the value of 13 Å. On the contrary, considering that the PAAm presents a draining effect and using in Eq. 2 $\Phi = 1.14 \times 10^{23}$, obtained from Eq. 1 with $a = 0.65$, we obtain $A = 20$ Å. This value of A is more plausible than the value of 13 Å for a vinyl polymer with a lateral group in his monomer.

Polycaprolactam

Tuzar et al. [23] has been studied this polyamide in the organic solvent *m*-cresol and in the mixture of 2,2,3,3-tetrafluoropropanol with 10% water and lithium chloride (TFP–H_2O–LiCl). With the viscometric results of Ref. 23, we apply the SFB equation (Eq. 3) and we obtain the two curves of Fig. 4. From the extrapolation to $M = 0$ we obtain $K_\theta = 40.5 \times 10^{-2}$ cm^3 gr^{-1} in the organic solvent (Curve A) and $K_\theta = 17 \times 10^{-2}$ cm^3 gr^{-1} in the mixture containing 10% water (Curve B).

With $\Phi = 2.6 \times 10^{23}$, in the two solvents, we obtain for the Kuhn statistical segment length, with the above two values of K_θ, and with $M_L = 13$ gr mol^{-1} Å^{-1}, $A = 17.5$ Å in metacresol and $A = 9$ Å in the mixture TFP–H_2O–LiCl. Considering now that this polyamide presents a draining effect in the containing 10% water mixture and obtaining Φ from Eq. 1 ($\Phi = 0.99 \times 10^{23}$ with $a = 0.76$) we obtain $A = 18.5$ Å. This value is close to the value of A obtained in the organic solvent.

Poly-4-vinylpyridine

We apply the SFB and the DB equations (Eqs. 3 and 4) with the viscometric results obtained by Berkowitz et al. [24] on fractions of poly-4-vinylpyridine (P4VP) dissolved in absolute ethanol and with the viscometric results obtained by Boyes and Strauss [25] on fractions of the same polymer dissolved in butanone–isopropanol mixture (86–14) and in ethanol–water mixture (92–8 by weight). The obtained values of K_θ are given in Table 1.

From the K_θ values, using Eq. 2, we have obtained the Kuhn statistical segment length, A, of P4VP in these solvents using $\Phi = 2.6 \times 10^{23}$ (Table 1). In the mixture containing water, the obtained value of A with $\Phi = 2.6 \times 10^{23}$ is equal to 11 Å. This value is very low for a vinyl polymer with a phenyl group on each monomer. If

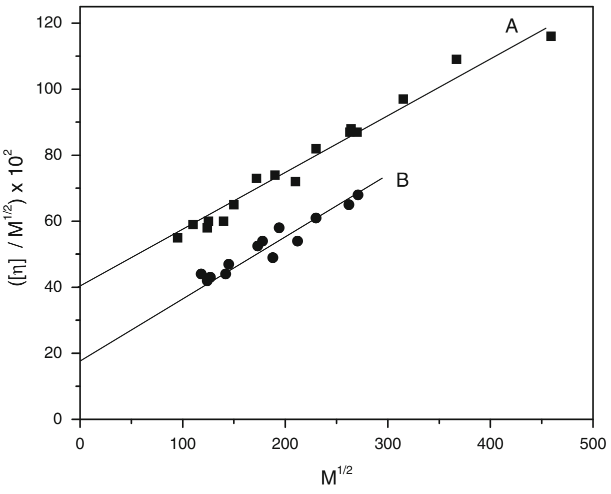

Fig. 4 SFB blots for polycaprolactam in organic solvent (*m*-cresol), curve *A*, and in a mixture containing 10% H_2O, curve *B*

we consider now that in the mixture containing water we have the appearance of draining effect, and using a Φ value obtained from Eq. 1, we obtain $A = 20$ Å. This value is the same with the values of A obtained in the other two solvents which do not contain water (Table 1).

Denaturated proteins

We have shown [4] that the denaturated proteins present a draining effect in aqueous salt solutions. Taking Φ from Eq. 1, we obtain for their statistical segment length a value of 24 Å while Flory and co-workers have obtained 23 Å. With $\Phi = 2.6 \times 10^{23}$ we obtain $A = 12$ Å (Table 1).

DNA

DNA must present a draining effect for two reasons: it is a very rigid macromolecule and is dissolved in the water. Indeed if we do not correct the value of Φ via Eq. 1, the obtained values of its statistical segment length are erroneous.

Presenting the variation of $\log[\eta]$ versus $\log M$ (MHS equation) for DNA fractions in the molecular mass region between 5 and 70×10^6 [26–28], we obtained a straight line with a slope equal to 0.73 and from Eq. 1 we obtain $\Phi = 1.08$. With the same viscometric results we apply the DB equation (Eq. 4) and we obtain the straight line of Fig. 5. The inverse of the slope of this straight line is equal to 1.66 or $K_\theta = 1.66$ cm^3 g$^{-3/2}$ mol$^{-1/2}$. With this value of K_θ and with the "constant" value of Φ ($\Phi = 2.6 \times 10^{23}$), we obtain from Eq. 2 for the statistical segment length of DNA the value of 650 Å, while the proposed values from different laboratories lie around of 1.100 Å. Using now for Φ the value of 1.08×10^{23}, obtained from Eq. 1, and with $M_L = 195$ gr mol^{-1} Å^{-1}, we obtain from Eq. 2, $A = 1.200$ Å.

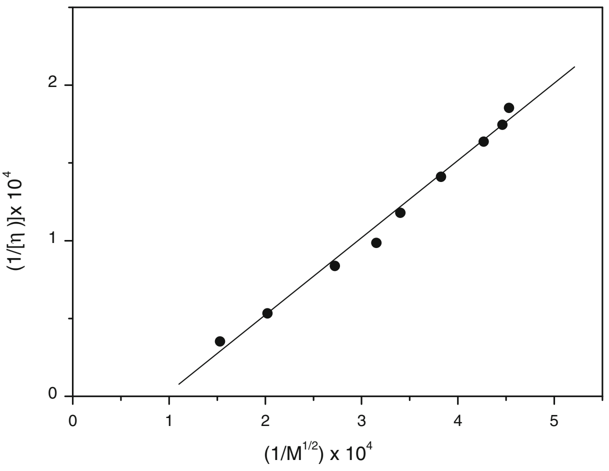

Fig. 5 DB plot for DNA in water

Conclusion

As we see in Table 1, if we use a value of Φ equal to 2.6×10^{23} for the polymers dissolved in water, we obtain very low values for their statistical segment length. Nevertheless, in water these polymers present a good solubility: exponent of the MHS equation enough higher from 0.5. Therefore, there is not reason for presenting such low values of their statistical segment length. On the contrary, the obtained values for the statistical segment length of the same polymers dissolved in water and using the parameter Φ which is given by Eq. 1, are almost the same with those when the polymers are dissolved in organic solvents. In this case, Φ is equal to 2.6×10^{23}, while draining effect is insignificant.

We have also shown that a value of Φ obtained from Eq. 1 is necessary, when we present the hydrodynamic volume of a polymer dissolved in water by $[\eta]M/\Phi$ (according to the Fox–Flory equation). Only with this value of hydrodynamic volume, we obtain a good applicability of the modified universal calibration of the gel permeation chromatography [6].

All the results presented in this study claim in favor that any flexible polymer dissolved in water presents a significant draining effect, and that this effect increases (decrease of the Φ value) when the quality of the solvent increases.

Finally, we must indicate that despite their draining effect, the polymers dissolved in water should still be considered as random coiled structures, because, as we have seen, they obey most of the structure properties relationships proposed for the polymers dissolved in organic solvents.

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