The unperturbed conformation and interaction parameters of polyvinylalcohol in aqueous solutions. Polydispersity effects

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Introduction

The conformation and other solution properties of a series of polymer homologs are usually characterized by two basic parameters, one of which is a measure for the unperturbed dimensions of the molecules and the second describing the polymer-solvent interactions. Parameters of the first kind are, e. g., the steric factor, σ, (1) the characteristic ratio, C, (2, 3) and the polymer constant, K_0 (1, 4). For the second parameter the linear expansion factor, α, (4, 5) the polymer-solvent interaction parameter, χ, (5) and the exponent a of the Mark-Houwink-Sakurada (MHS) equation ($[\eta] = K M_v^a$) are in use. Within each group the parameters are interrelated, as will be shown below.

To obtain these parameters most common practice involves viscometry (1, 4–6) of dilute solutions of polymers as a function of molecular weight. The resulting intrinsic viscosity-molecular weight data can be plotted in several ways (1, 7–10) to obtain pairs of the above characteristics, for instance K_0 and χ. Of these plotting methods that of Burchard-Stockmayer-Fixman (8, 9) (BSF) is most convenient. A derivation and discussion of the BSF equation will be given in order to revive the special form of the equation in the case of polydisperse polymers and to review its abilities and limitations.

For many polymers literature values of the aforementioned parameters have been compiled (1, 11, 12), also for *polyvinylalcohol* (PVA). However, as for many other polymers the data of PVA are based upon experiments with polydisperse, ill-defined fractions and the appropriate polydispersity corrections have not been made. The results of Matsumoto and Ohyanagi

(13) (see also Pritchard (14) and Kurata et al. (1, 2)) make an exception, but these authors have calculated only the coefficient K and exponent a of the empirical MHS equation. In the present study, the original data of Matsumoto and Ohyanagi have been used to construct a BSF plot and to obtain K_0 and χ for aqueous PVA solutions. We also include some new experimental data on several commercially available PVA samples of different origin.

Results have been discussed on the basis of a comparison of the present BSF plot with similar plots based on other literature data of PVA.

The Burchard-Stockmayer-Fixman relation

According to the Kirkwood-Riseman (15) theory of viscous flow including hydrodynamic interaction, the intrinsic viscosity, $[\eta]_0$, of an unperturbed linear flexible chain of n bonds may be written as

$$[\eta]_0 = \Phi(X) <h^2>_0^{3/2} M^{-1} \qquad [1]$$

with

$$\Phi(X) = (\pi/6)^{3/2} N_{Av}[XF(X)] \qquad [2]$$

and

$$<h^2>_0 = Cnl^2 \qquad [3]$$

where $<h^2>_0$ is the unperturbed mean square end-to-end distance, l the bond length, C the characteristic ratio, M the molecular weight of the polymer and N_{Av} Avogadro's number. $\Phi(X)$ is a dimensionless quantity which is related to

the extent of drainage, X. Revised values of the function $XF(X)$ have been tabulated (4). As shown by Flory (5), Kurata and Stockmayer (1) and Yamakawa (4) there is no evidence for partial draining of the solvent through the polymer coils. Therefore $X \to \infty$ and $XF(X) = 1.259$. In that case $\Phi(\infty)$ is a universal constant, generally denoted as Φ_0, the viscosity constant with a theoretical value 2.86×10^{23} (4, 16). The best experimental value of Φ_0, based on viscosity and light scattering measurements, is $(2.5 \pm 0.1)10^{23}$ (2, 4). Flory (2) suggests the value 2.6×10^{23}. For $X \to \infty$ equation [1] can be written as

$$[\eta] = K_0 M^{1/2} \qquad [4]$$

with K_0 a polymer constant (unperturbed dimensions), defined as

$$K_0 \equiv \Phi_0 <h^2>_0^{3/2} M^{-3/2} = \Phi_0 (Cl^2/M_0)^{3/2}$$
$$\equiv \Phi_0 A^3 \qquad [5]$$

showing also the relation between K_0 and C. M_0 is the molecular weight per bond. The square root of the cluster of constants Cl^2/M_0 is often denoted as A.

All of this applies to θ-conditions. However, under non-θ-conditions flexible chains have perturbed dimensions and equations [1] and [4] should be modified as

$$[\eta] = \Phi_0 <h^2>_0^{3/2} \alpha_\eta^3 M^{-1} = K_0 \alpha_\eta^3 M^{1/2} \qquad [6]$$

with

$$\alpha_\eta^3 \equiv [\eta] [\eta]_0^{-1} \qquad [7]^{*)}$$

Kurata and Yamakawa (17) were the first to derive a theoretical expression for α_η^3

$$\alpha_\eta^3 = 1 + 1.55 z + \ldots \qquad [8a]$$

with the excluded volume parameter z defined as

$$z = 0.330 \, BA^{-3} \, M^{1/2} \qquad [9]$$

A is defined in [5] and B is a measure for the polymer-solvent interactions related to the specific polymer volume V and the Flory-Huggins interaction parameter χ by (4)

$$B = V^2 (1-2\chi) (v_1 N_{Av})^{-1} \qquad [10]$$

with v_1 the molar volume. The solvent. Equation [8a] is a first order approximation and applies only for small values of z. In subsequent studies (16, 18–21) several other approximations of α_η have been reported, giving values for the coefficient of z ranging from 1.80 to 1.06. Most recently Shimada and Yamakawa (16) calculated a value of 1.14. Hence, in general [8a] can be written as

$$\alpha_\eta^3 = 1 + C_1 z + \ldots \qquad [8]$$

Experimental light scattering and viscometry results (4, 22, 23) suggest that the coefficient of z is between 1.06 and 1.55. Higher values of C_1 definitely overestimate α_η.

Combination of equations [6], [8] and [9] results in the BSF relation:

$$[\eta] = K_0 M^{1/2} + 0.330 \, C_1 \, \phi_0 BM. \qquad [11]$$

The first term of the RHS of [11] equals [4] and represents the intrinsic viscosity in the unperturbed state. The second term accounts for the polymer-solvent interactions and for the own volume of the polymer. Plotting $[\eta]/M^{0.5}$ against $M^{0.5}$ for a series of *monodisperse* polymer homologs should result in a straight line, from which K_0 and B can be found.

A discussion of the BSF relation and the reliability of the derived parameters K_0 and B, also in relation to alternative methods (1, 7, 10) to deduce K_0 and B from viscometry, has been given by several authors (4, 10, 22). Generally the validity of [11] is limited to small expansion factors, as expected from the restriction on [8]. However, Stacy and Arnett (24) found also in good solvents correct values for K_0. Other methods offer mainly an improvement for large M and/or α_η. Below molecular weights of about 10,000 the BSF relation gives usually incorrect results. This may have two causes: random flight statistics are no longer applicable, and the assumption that no drainage of the polymer occurs is no longer valid.

So far, the discussion has not included *polydispersity effects*. However, almost all poly-

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*) Empirically α_η^3 can be written also as $\alpha_\eta^3 = kM^\varepsilon$. Substitution of this relation in [6] gives the MHS equation with $a = \varepsilon + 0.5$ and $K = kK_0$.

mer samples or fractions are considerably polydisperse. In order to account for this effect the derived equations have to be modified and average quantities have to be introduced. The way of averaging the various molecular weight dependent quantities should be consistent. For a polydisperse sample composed of monodisperse fractions i with intrinsic viscosity $[\eta]_i$ and concentration c_i, one can write

$$[\eta] = \frac{\eta_{re}}{c_p} = \frac{\sum_i c_i [\eta]_i}{\sum_i c_i} \quad (c_p \to 0)$$

with η_{re} the viscosity ratio excess and c_p the total polymer concentration. Inserting this into [11] gives

$$[\eta] = K_0 \frac{\sum_i c_i M_i^{1/2}}{\sum_i c_i} + 0.330 C_1 \phi_0 B \frac{\sum_i c_i M_i}{\sum_i c_i} \quad [12a]$$

or

$$[\eta] = K_0 (M_{v.5})^{1/2} + 0.330 \, C_i \phi_0 B M_w \quad [12b]$$

where M_w is the weight average molecular weight and $M_{v.5}$ the viscometric average molecular weight with $a = 0.5$ $[M_{va} = (\sum c_i M_i^a / \sum c_i)^{1/a}]$. The average viscosity expansion factor follows from

$$<\alpha_\eta>^3 = [\eta]/K_0 M_{v.5}^{1/2} . \quad [13]$$

Equations [12] has been presented in a more complicated form before (1). The advantage of the present notation is that it clearly shows that in the first and second term of the RHS of equations [12] two *different molecular weight averages* appear. In general, these averages can be computed only if the molecular weight distribution is known.

In the case that improper average molecular weights are used the obtained parameters still contain polydispersity contributions. For instance, when the BSF relation would be used with number average molecular weights (M_n), it would read

$$[\eta] = K_0^* M_n^{1/2} + 0.330 \, C_1 \phi_0 B^* M_n$$

whereas the correct equation should be

$$\begin{aligned}[\eta] = K_0 \left(\frac{M_{v.5}}{M_n}\right)^{1/2} M_n^{1/2} \\ + 0.330 \, C_1 \phi_0 B \left(\frac{M_w}{M_n}\right) M_n \end{aligned} \quad [14]$$

If, in this case, experiments are performed with polymer fractions and each fractions happens to have the same molecular weight distribution, then the polydispersity corrections $(M_{v.5}/M_n)^{0.5}$ and M_w/M_n are constants and the errors depend on the molecular weight distribution of the fractions. For instance, for a series of polymers having an exponential or a log-normal distribution (12) with $M_w/M_n = 2$ and $(M_{v.5}/M_n)^{0.5} \approx 1.3$ B^* is in error by a factor of 2 and K_0^* exceeds K_0 by 30%. When the fractions differ with respect to their molecular weight distribution, a straight BSF plot is solely due to fortuitous compensation.

Materials and methods

Several commercial PVA's of different origin have been analyzed. Samples were obtained from Konam (Amsterdam), Wacker (FRG) and Kuraray (Japan). In industrial practice complete hydrolysis of the precursor polyvinylacetate is seldom achieved and the selected samples contain about 2 mole % of acetate groups. *Molecular weight distributions* of these samples were obtained by gel permeation chromatography (GPC), using a Waters Associates model 200 GPC chromatograph. The experimental conditions have been given elsewhere (25). Since well-defined narrow molecular weight fractions of PVA were not available, the columns were calibrated with highly monodisperse polystyrene (PS) samples from Pressure Chemical Company, Pittsburg. Following Grubisic et al. (26) and Coll and Gildings (27) it was assumed that the hydrodynamic volume of the molecules controlled the separation. The relation between M_{PS} and M_{PVA} was found using the method of Dawkins (28). No corrections were made for the Gaussian peak broadening due to the imperfection of the instrument. Calculated average molecular weights and polydispersity coefficients are shown in table 1.

The variability in the molecular weight distribution over the various fractions is much larger for Polyviol than for Poval and Konam samples. Probably, this is caused by the different polymerization methods employed for the Polyviol samples: for V03/20 a bulk polymerization process was used, whereas V13/30 and W48/20 were prepared by solution and suspension polymerization respectively (29, 30). In contrast, the Poval (31) and Konam (32) samples are all prepared by continuous solution polymerization. The width of their molecular weight distribution is affected only by the different degrees of conversion (5) and these result only in relatively small differences in the distribution width.

At room temperature even dilute aqueous PVA solutions may form aggregates due to intermolecular hydrogen bonds (14, 33). However, PVA solutions are reasonably stable if the acetate content is 1 to 2% (34). Branching in PVA molecules is small, because most side chains present in the precursor polyvinyl acetate split off during saponification (14, 35, 36).

Viscometry experiments of freshly prepared dilute PVA solutions were made with Ubbelohde precision viscometers (KPG, Jenaer Glaswerk, Schott Mainz) at 30.00 ± 0.02 °C. Solutions were filtered before use. All measurements were

Table 1. Molecular weights ($g \cdot mol^{-1}$) and polydispersity coefficients of the commercial PVA samples as obtained by GPC.

Manufacturer	code	M_n	M_w	$M_{v.5}$	M_w/M_n	$(M_{v.5}/M_n)^{0.5}$	$[\eta]$ ($dm^3 \cdot g^{-1}$)
Kuraray	105	21,000	46,500	38,500	2.2	1.36	0.0417
(Poval)	117	63,000	145,000	117,000	2.3	1.37	0.0823
	124	88,000	209,000	168,500	2.4	1.39	0.1036
Komam	16–98	59,000	135,000	109,000	2.3	1.36	0.0813
	60–99	79,500	191,000	152,000	2.4	1.38	0.1024
Wacker	V03/20	13,000	31,500	26,000	2.4	1.41	0.0318
(Polyviol)	V13/20	39,000	135,000	100,500	3.5	1.61	0.0729
	W48/20	39,000	226,500	160,000	5.8	2.03	0.1037

performed in the concentration range of 2 to 10 g dm^{-3}. Each series contained at least four concentrations and each measurement was duplicated with a capillary of different radius. Couette and kinetic corrections were applied in accordance with the tables supplied with the viscometers. Density and shear corrections were neglected. The intrinsic viscosity, $[\eta]$, of each PVA sample was calculated from a Martin plot. According to Sakai (37) this gives reliable results for poor solvents, as is water for PVA. The applicability of the Martin plot for aqueous PVA solutions was demonstrated by Scholtens (38). Obtained intrinsic viscosities are shown in table 1. Viscosity average molecular weights calculated with the MHS equation using the constans (13) $K = 4.53 \times 10^{-5}$ dm$^{-3} \cdot$g^{-1} and $a = 0.64$ agreed well with those calculated from GPC.

Results and discussion

Matsumoto and Ohyanagi (13) have measured the viscosity of freshly prepared aqueous PVA solutions at 30 °C, using PVA samples obtained from low (<10%) conversion polyvinylacetate. Molecular weights were determined by light-scattering and end-group analysis indicating that for their samples $M_w/M_n \approx 2$. From this, and the fact that a low conversion solution polymerization was used, Matsumoto and Ohyanagi have concluded that the molecular weight distribution of their samples could be represented by the "most probable" or "Flory" distribution (5). According to this distribution the ratios of the average molecular weights M_n, M_{va} and M_w follow from

$$M_n:M_{va}:M_w = 1:[(1+a)\Gamma(1+a)]^{1/a}:2 \qquad [15]$$

where Γ is the gamma function and a the exponent of M in the definition of the viscometric average molecular weight. Due to their preparation method, branching of the samples should be absent or small. The degree of hydrolysis is not stated explicitly, but it probably exceeds 99.5%.

The viscosity data of Matsumoto and Ohyanagi cover a wide range of molecular weights and are corrected to zero rate of shear for samples with $M_w > 150,000$. Intrinsic viscosities given by these authors were obtained from a Huggins plot (39). According to Sakai (37) in not too good solvents a Huggins plot underestimates $[\eta]$ somewhat, but for aqueous PVA solutions the error introduced in this way will be probably $\leq 2\%$ (38).

Intrinsic viscosities and weight average molecular weights as obtained by Matsumoto and Ohyanagi (MO) are shown in table 2. Viscosity average molecular weights, $M_{v.5}$ ($a = 0.5$), calculated with [15] are also given.

Using the intrinsic viscosity-molecular weight data of tables 1 and 2, we constructed a BSF plot according to equation [12]. The agreement between our results for the commercial PVA's and

Table 2. The original intrinsic viscosity-weight average molecular weight data of Matsumoto and Ohyanagi (13) and $M_{v.5}$, $<a_\eta>$ and $<z>$ as calculated from equations [15], [13] and [8] respectively ($C_1 = 1.14$)

| $[\eta]$ ($dm^3 \cdot g^{-1}$)	M_w ($g \cdot mol^{-1}$)	$M_{v.5}$	$<a_\eta>$	$<z>$
0.229	650,300	574,900	1.25	—
0.220	619,500	547,700	1.24	—
0.215	583,400	515,800	1.25	—
0.179	432,100	382,000	1.23	—
0.168	354,600	313,500	1.25	—
0.169	352,900	311,900	1.25	—
0.124	248,200	219,400	1.20	—
0.0889	146,100	129,100	1.17	0.53
0.0740	102,100	90,200	1.17	0.53
0.0499	59,100	52,300	1.12	0.35
0.0246	19,200	17,000	1.06	0.16
0.0585	77,900	68,800	1.13	0.38
0.0326	29,400	26,000	1.09	0.26
0.0259	21,700	19,200	1.06	0.16
0.0201	13,700	12,100	1.06	0.16
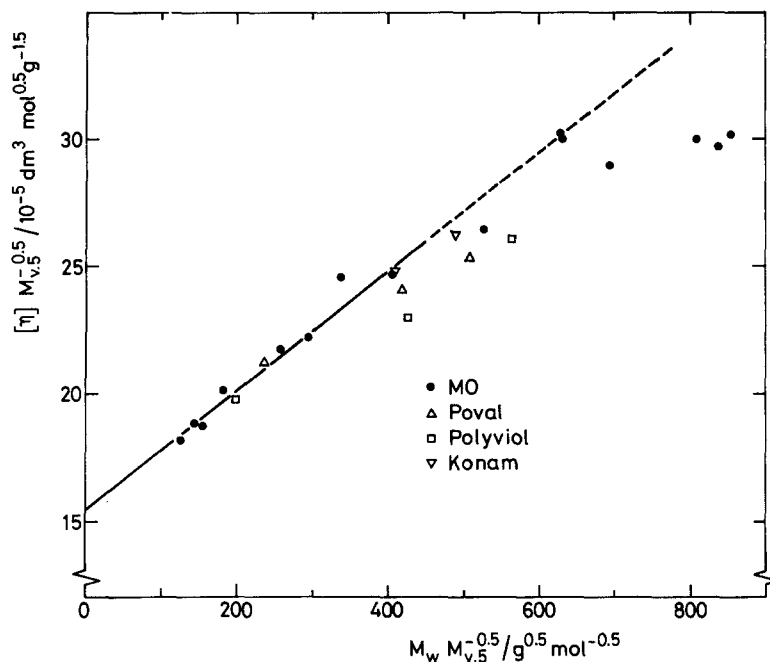
Fig. 1. Burchard-Stockmayer-Fixman plot for PVA, covering a wide molecular weight range

those obtained with Matsumoto and Ohyanagi's data is reasonably good, except for Polyviol V13/20 which may be due to an error in the polydispersity coefficient of this PVA. Generally, it may be concluded that the same BSF plot applies to PVA's of quite different nature and polydispersity. The BSF plot of figure 1 shows a linear behaviour up to molecular weights of about $M_w = 150,000$; extrapolation of the curve to higher molecular weights would overestimate α_η^3 considerably. In contrast with the BSF plot, the MHS plot (given by Matsumoto and Ohyanagi) is linear over the complete molecular weight range studied; moreover the spread about the MHS curve is less. Similar differences between a BSF and a MHS plot have been reported by Garvey et al. (40) studying polyvinylalcohol samples containing 12 mole% acetate groups.

To demonstrate the effect of polydispersity on a BSF plot, results were recalculated with the inappropriate molecular weight averages M_n and M_w, see figure 2. The correct BSF curve is plotted as a reference. The error introduced by using M_n is very large (compare also eq. [14]). Moreover, the results for the commercial samples, especially in the case of Polyviol, differ more strongly from the correct result than those

based on Matsumoto and Ohyanagi's data. This is related to the fact that the samples used by these authors are the least polydisperse. The very large deviations observed for Polyviol are due to the strong increase in polydispersity with increasing molecular weight. Similar, but small-
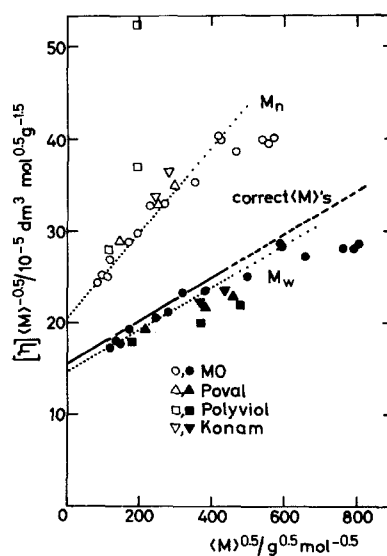

Fig. 2. The effect of using M_n or M_w instead of the correct molecular weight averages for the construction of a BSF plot

Table 3. Conformation and interaction parameters of PVA in aqueous solution. B and χ depend on the coefficient C_1 in equations [8] and [12].

K_0 dm$^3 \cdot$mol$^{0.5}$ g$^{-1.5}$	A nm$\cdot$mol$^{0.5}$ g$^{-0.5}$	C	σ	C_1	B dm$^3 \cdot$mol$\cdot$g^{-2}	χ
15.5 10^{-5}	0.084	6.6	1.82	1.06	2.56×10^{-30}	0.477
				1.14	2.38×10^{-30}	0.478
				1.55	1.75×10^{-30}	0.484

er, errors are made when M_w is used, and the deviation of K_0 from the correct value is still serious.

The values of K_0 and B found from figure 1 are shown in table 3, together with those of C, A and $\sigma[=(C/2)^{0.5}]$, corresponding with K_0 and χ derived from B.

The latter two parameters depend on the coefficient C_1 in equation [8]. Results for three different theoretical values of C_1 are tabulated (16, 17, 20). For Φ_0 the value 2.6×10^{23} was taken. χ was found from [10], substituting $V = 0.77 \times 10^{-3}$ dm$^3 \cdot$g^{-1} (41), $v_1 = 18 \times 10^{-3}$ dm$^3 \cdot$mol^{-1}, and $N_{Av} = 6.02 \times 10^{23}$ and the corresponding B value. The values of χ given in table 3 are based on [η], therefore they correspond to an (extrapolated) zero volume fraction of PVA.

Independent measurements of χ based on osmotic (42) and vapour pressure (43) data have resulted in $\chi = 0.494$ for semi-dilute PVA solutions at 30 °C. This value has been taken as a reference value of further calculations by Peppas and Merrill (44) in their study of χ as a function of temperature and volume fraction of PVA. Extrapolation of the χ (volume fraction) curve at 30 °C given by Peppas and Merrill to zero volume fraction PVA results in $0.477 < \chi < 0.480$. These values correspond closely to the viscometric χ value, which is obtained with $C_1 = 1.14$ or 1.06. Apparently, the coefficient 1.55 is incorrect for the PVA-H$_2$O system. A similar conclusion was obtained by Yamakawa (4) for various other polymer-solvent systems. Hence, giving preference to the most recent theoretical value of C_1, our conclusion is that equation [8] should read:

$$\alpha_\eta^3 = 1 + 1.14 \, z + \ldots \qquad [8]$$

Consequently, the BSF relation should be written as:

$$[\eta] = K_0 (M_{v.5})^{1/2} + 0.38 \, \phi_0 B M_w. \qquad [12]$$

From K_0 and equations [13] and [8], $<\alpha_\eta>$ and $<z>$ can be calculated. Results are collected table 2. Up to about $<\alpha_\eta> = 1.17$ and $<z> = 0.5$ the BSF plot is linear; beyond this region higher terms in z play a role, in agreement with the fact that [8] is a first-order approximation for small values of z. The downward deviation from the straight line in figure 1 is predicted by theory, since the coefficient of z^2 in the series expansions of α_η is negative (4). In principle, the deviation of the straight BSF plot at larger values of α_η can also be partly due to some draining of solvent through the polymer coil as a consequence of its expansion. However, the expansion is still relatively small, and it does not seem likely that this effect is dominating. Although branching of the samples is small, some branching in the higher molecular weight samples could also partly cause the observed deviation of the straight BSF-plot. Generally, it may be concluded from figure 1 that a BSF plot of PVA constructed mainly with samples in the region of high molecular weight easily overestimates K_0 and χ.

To be able to apply random flight statistics to a regular flexible chain, Kuhn (45) postulated the concept of the *"equivalent chain"* consisting of statistical chain elements (*sce*). For a vinyl chain, assuming a distance of 0.253 nm between the alternate carbon atoms (46) the length, L, of a *sce* is equal to 0.187 C (nm) and the number of bonds per *sce*, $N = 1.48\,C$. For PVA with $C = 6.6$, L becomes 1.23 nm and $N = 9.8$.

Comparison with other literature data

Finally we wish to compare our results with previous literature data. Kurata et al. (1, 12) have based their calculations of K_0 upon results of Flory and Leutner (47), Nakajima and Furutate (42) and Dieu (48). The experimental data of Dieu are somewhat dubious and cover only

three samples differing in molecular weight. The results deviate seriously from other findings, see figure 3. Nakajima and Furutate (42) have measured intrinsic viscosities and number average molecular weights of crude PVA fractions to establish MHS constants. Their results coincides with the MHS relation for PVA as found by Matsumoto and Ohyanagi (13) using M_n. It might be expected therefore that a BSF plot of these data, in which the polydispersity is taken into account, would be close to the present results. Unfortunately, the polydispersity is unknown, so that further verification is impossible. Flory and Leutner (47) also determined number average molecular weights of fractionated PVA samples. With their data a crude BSF plot, based on M_n and $[\eta]$, has been constructed in figure 3. The slope of this plot is rather steep and differs strongly from our result, which might be due to the use of M_n (see eq. [14] or fig. 2). This suggests that in spite of the fractionation the samples of Flory and Leutner were still rather polydisperse. Another explanation could be that the fractionation was affected by secondary structural effects in the PVA chain.

Viscosity molecular weight data for PVA have also been given by Beresniewics (49) and Wolfram and Nagy (50). To calculate M_v of the PVA fractions, the latter authors used MHS constants found by Matsumoto and Ohyanagi which were based on M_w. Consequently, incorrect values of

M_v have been obtained. To find the correct values, we recalculated viscosity average molecular weights with the appropriate MHS equation. These values of M_v were combined with the intrinsic viscosities to a BSF plot, see figure 3 (x). The agreement with our own BSF plot is very good. Partly, this might be due to the fact that the MHS constants of Matsumoto and Ohyanagi were used to obtain M_v, which introduces some circuity into the argument.

A BSF plot based on the results of Beresniewics (49) is also shown in figure 3. Molecular weights of the fractionated PVA samples have been determined by viscometry using a MHS equation corrected for polydispersity, with constants $a = 0.63$ and $K = 5.95 \times 10^{-5}$ dm$^3 \cdot$g^{-1}. The slope of the obtained BSF plot is about the same as it is for our results, but K_0 is somewhat larger. Again only M_v is known, so that polydispersity corrections could not be applied. Incorporation of these corrections could bring the results of Beresniewics closer to our BSF curve.

In conclusion, the value $K_0 = 15.5 \times 10^{-5}$ dm$^3 \cdot$mol$^{0.5} \cdot$g$^{-1.5}$ is not really contradicted by K_0 values obtained with other literature data on PVA. In the author's opinion, the present value is definitely better than the values given in reviews by Kurata et al. (1, 12) and Van Krevelen (11), viz. $(22.5 \pm 2.5) \times 10^{-5}$ and $(19 \pm 3) \times 10^{-5}$ respectively. This is substantiated by the fact that the present K_0 and the ensuing values of C and σ (see table 3) compare much better with those of other simple vinyl polymers such as polyethylene or propylene (51, 2) than Kurata's or Van Krevelen's values do.

Except for Flory's result, the slopes of the BSF plots agree mutually rather well, lending support to the values of B and χ reported in table 3. In view of the discussion given above, for low polymer concentrations and 30 °C we consider 0.478 as the most reliable value for the polymer-solvent interaction parameter χ. Therefore, it may be concluded that water is only a poor solvent for PVA.

Conclusions

In order to obtain values of K_0 and χ from a BSF plot, two different molecular weight averages, viz. $M_{v.5}$ and M_w, have to be used; see equation [12].
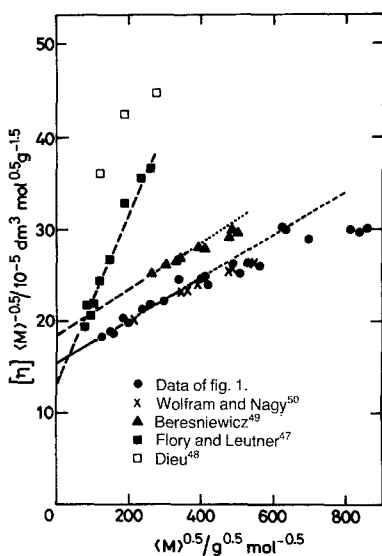

Fig 3. Comparison of BSF plots for PVA based upon the results of several authors

The first-order perturbation coefficient in the series expansion of the cubed viscosity radius expansion factor, α_η^3, should be 1.14 instead of 1.55.

The constant K_0 of PVA and the Flory-Huggins interaction parameter, χ, for aqueous PVA solutions have been obtained from a BSF plot corrected for polydispersity. The results are $K_0 = 15.5 \times 10^{-5} \ dm^3 \cdot mol^{0.5} \cdot g^{-1.5}$ and $\chi = 0.478$ (30 °C, $c_p \to 0$). Neglect of the polydispersity would have led to serious errors. K_0 is definitely smaller than previously reported values (1, 11, 12).

Summary

Unperturbed conformation and interaction parameters of polyvinyl alcohol in aqueous solutions have been determined. To this end intrinsic viscosity-molecular weight data have been analyzed in terms of the Burchard-Stockmayer-Fixman (BSF) equation. A special form of this equation for polydisperse polymers has been derived. Values of the Flory-Huggins interaction parameter χ, the polymer constant K_0 and other related quantities have been obtained using the original data of Matsumoto and Ohyanagi. For sake of comparison intrinsic viscosity-molecular weight data of several commercial PVA samples were measured and analyzed. The parameters obtained, are discussed in relation to other literature data of PVA. The viscosimetric χ value agrees very well with literature values of χ if the cubed viscosity radius expansion factor is given by the theoretical equation derived by Shimada and Yamakawa: $\alpha_\eta^3 = 1 + 1.14 z + \ldots$.

Zusammenfassung

Ungestörte Konformations- und Wechselwirkungsparameter von Polyvinylalkohol (PVA) in wäßriger Lösung wurden bestimmt. Dazu wurde die Beziehung zwischen der Grenzviskosität [η] und dem Molekulargewicht mit Hilfe der Burchard-Stockmayer-Fixman-Gleichung analysiert. Zuerst aber wurde eine besondere Form der BSF-Gleichung für polydisperse Polymere abgeleitet. Die gefundenen Werte für den Wechselwirkungsparameter χ und die Polymerkonstante K_0 wurden auf den originellen Daten von Matsumoto und Ohyanagi basiert. Zum Vergleich wurden verschiedene kommerzielle PVA-Muster analysiert. Die gemessenen χ-Werte stimmen mit den Literaturwerten für χ am besten überein, wenn für die Expansionskoeffizienten α_η die theoretische Gleichung von Shimada und Yamakawa $\alpha_\eta^3 = 1 + 1.14 z \ldots$ eingeführt wird. Die Ergebnisse wurden anhand weiterer Literaturdaten über PVA erörtert.

Key words

Polyvinylalcohol solution properties, unperturbed dimensions, viscometry, Burchard-Stockmayer-Fixman equation, polydispersity effects.

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