

Flexibility and hydrodynamic properties of poly(vinylpyrrolidone) in non-ideal solvents

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Abstract

At 298.15K, intrinsic viscosity $[\eta]$ has been measured for poly(vinylpyrrolidone), PVP, samples of different relative molar masses M in pure water and eight different binary solvents. These solvents were water/acetone mixtures having different volume fractions of acetone (ACT). The solvation power of these mixtures showed a cosolvency effect. The maximum solvation power was found for the mixture containing 0.2 volume fraction of ACT. The value of $K_{\theta} = 74 \times 10^{-3} \text{ dm}^3 \text{ kg}^{-1}$ was utilized for calculating the unperturbed dimensions, u.d., steric factor, σ , the characteristic ratio, C_{∞} , and the persistence length, a_p . Values of 0.666 Å, 2.28, 10.38 and 8.76 Å, respectively, were obtained for PVP in theta - solvent. The calculated values of the effective radius (R_e), effective unit length (b) and the effective hydrodynamic radius of monomeric unit (r_0) showed the complete impermeability of polymer molecules. Some errors in the polymer handbook and CRC, water-soluble synthetic polymers, were demonstrated with its logical corrections.

INTRODUCTION

In the last decade, water soluble polymers have found increasing commercial applications in mineral processing, pharmaceuticals, detergents, cosmetics, textile production [1], enhanced oil recovery [2], and for separation of protein mixtures [3,4].

The literature is rich in theoretical and experimental studies for describing the behaviour of poly(vinylpyrrolidone), PVP, in binary and ternary solutions by viscosity [5-9], light scattering [10-14], osmotic pressure [15] and refractometric [16] measurements. Unfortunately, many of these studies referred to some sources which are not absolutely correct, for instance, references 1,17 and 18.

In a recent article [9] we introduced a new method for deriving the unperturbed dimensions, u.d., of PVP from the viscosity data in cosolvent systems. In the present report we studied the equilibrium flexibility and the hydrodynamic properties of PVP in water/ACT binary mixtures. It was of interest also to highlight the incorrect information quoted in the polymer handbook (ref.17) and the other two references (refs 1,18), to eliminate the confusion we had met during our study.

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EXPERIMENTAL

Analytical grade ACT was distilled at atmospheric pressure. Deionized bidistilled water was employed as thermodynamically good solvent. Details of the preparation of binary mixtures, fractionation of PVP as well as measurement of $[\eta]$ have been described elsewhere [9,19,20]. However, eight water/ACT mixed solvents having volume fractions of ACT equal to 0.1,0.2,0.25,0.3,0.4,0.5,0.6 and 0.668 were made up volumetrically and denoted here as solvents b,c,d,e,f,g,h and i respectively. The pure solvent (water) was designated as solvent a. The PVP fractions were designated as PVP1-PVP7, where PVP1 possessed the highest molecular weight. The molecular weight of these fractions were given in our previous study [9].

RESULTS AND DISCUSSION

Intrinsic viscosity

The measured values of $[\eta]$ for the PVP samples (PVP1-PVP7) in water and water/ACT binary mixtures at 298.15 K are presented graphically in Fig.1. The logarithmic values of $[\eta]$ are plotted as a function of $\log M + \phi$ (ACT). The straight lines denoted as a-j represent the variation of $\log [\eta]$ with $\log M$. It is obvious that the maximum slope is obtained for line c which represents the volume fraction of acetone, $\phi(\text{ACT}) = 0.2$. The curves represent the variation of $\log [\eta]$ with $\phi(\text{ACT})$ for each molecular weight, increase with increasing $\phi(\text{ACT})$, passing through a maximum, then start to decrease. The maximum $\log [\eta]$, for each PVP fraction is attained when $\phi(\text{ACT}) = 0.2$. At this composition, the maximum solvation power was obtained and the Mark Houwink constant α , as it was given previously [9], is 0.86. The behaviour of this binary liquid system is considered as a good representation of the cosolvency effect. The minimum value of 0.5 for the Mark Houwink constant α was obtained in solvent i where the theta condition was confirmed [9]. Our previous results [9] showed that the theta composition of water/ACT, at 298.15 K, for PVP is $\phi(\text{ACT}) = 0.668$. This value was found to be in good agreement with the values obtained by Meza and Gargallo [18] and by Elias [21,22]. However, Molyneaux [1] has reported that the water/ACT mixture having volume fraction of water $\phi(\text{H}_2\text{O}) = 0.67$ is the theta - solvent for PVP and attributed this information to Elias [21,22] and Meza and Gargallo [18]. The original papers of Elias [21,22] stated that water/ACT mixture at which the ratio of water to ACT, by volume = 0.497 is the theta -solvent. This ratio which is equivalent to 0.332, for the volume fraction of water, is similar to that reported by Meza and Gargallo [18]. It is obvious that the volume fraction of the components of the mixed solvent has been reversed in Molyneaux book [1] and the correct composition, according to the original sources, is $\phi(\text{H}_2\text{O}) = 0.332$ and not 0.67.

Flexibility of the polymer chains

The equilibrium flexibility of the polymer chains are evaluated in terms of the conformational ratio, σ , which is the ratio of the root-mean-square unperturbed end-to-end distance $\langle r_{20}^2 \rangle^{1/2}$ of a polymer chain to the value $\langle r_{2cf}^2 \rangle^{1/2}$ for a corresponding Gaussian chain having completely free rotation about bonds connected by fixed valence angle, i.e.

$$\begin{aligned} \sigma &= (\langle r_{20}^2 \rangle / M)^{1/2} / (\langle r_{2cf}^2 \rangle / M)^{1/2} \\ &= (\langle r_{20}^2 \rangle / \langle r_{2cf}^2 \rangle)^{1/2} \dots \dots \dots (1) \end{aligned}$$

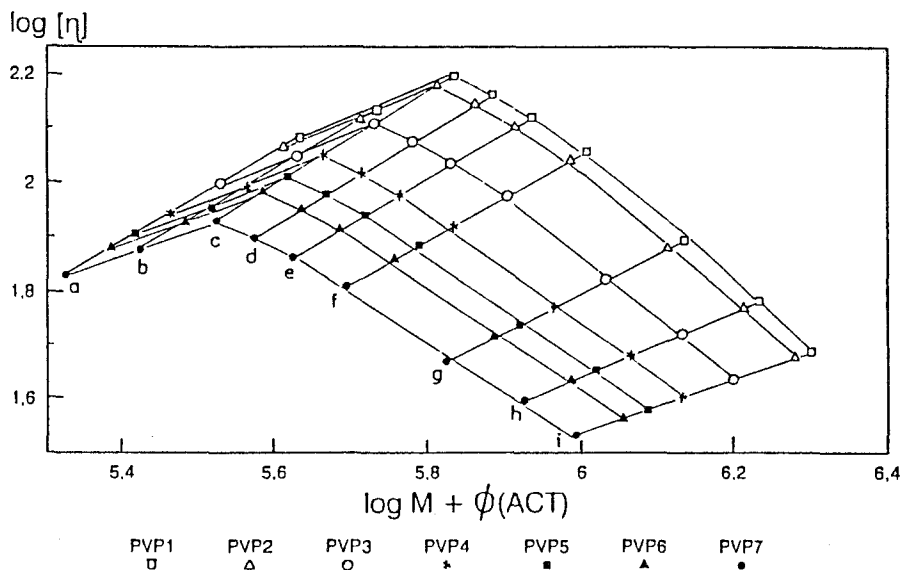


Fig.1 Viscosity data at different volume fractions of acetone

Flory [23] has calculated completely and accurately the effect of short-range interactions on the dimensions of random-coil polymers. He showed that, the restriction to fixed bond angle θ expands the chain by a factor of $[(1-\cos \theta)/(1+\cos \theta)]^{1/2}$, equal to $\sqrt{2}$ for carbon-carbon bonds. Consequently, the freely-rotating dimension of a chain consisting of only one kind of bonds is expressed as

$$\langle r_{of}^2 \rangle = nl^2 (1-\cos\theta)/(1+\cos\theta).....(2)$$

where n is the number of bonds, l is the bond length, θ is the bond angle. For polymethylene chain $\theta=109.5^\circ$ and $l=1.54 \text{ \AA}$ for C-C bond. Kurata et al.[17] and Meza and Gargallo[18] reported Eqn.3 for calculating the freely-rotating dimension

$$\langle r_{of}^2 \rangle = nl^2 (1+\cos\theta)/(1-\cos\theta).....(3)$$

They assigned the values of $\theta=109.5^\circ$ ($\cos\theta=1/3$) and $n=2M/M_0$ are the molecular weight of the polymer and the monomer respectively. From Eqn.3 they arrived to

$$\langle r_{of}^2 \rangle = 3.08 M^{1/2}/M_0^{1/2}.....(4)$$

and for PVP the freely-rotating dimension was driven by Meza and Gargallo [18] to be $0.290 \text{ \AA} M^{1/2}$. As far as we know, $\cos 109.5^\circ$ ($\cos \theta$) = $-1/3$ and not $1/3$. Invoking the correct value of $\cos\theta = -1/3$, Eqn 3 yields

$$\langle r_{of}^2 \rangle^{1/2} = 1.539 M^{1/2}/M_0^{1/2}.....(5)$$

and consequently $\langle r_{of}^2 \rangle^{1/2}$ for PVP = $0.146 \text{ \AA} M^{1/2}$. Under this condition, equation 3 shows that the restriction to fixed bond angle θ expands the

chain by a factor $[(1+\cos \theta)/(1-\cos \theta)]^{1/2}$, equaling $\sqrt{0.5}$. It is obvious that using $\cos \theta=1/3$, in references 17&18, compensated the error in Eqn 3, which must be corrected to have the form of Eqn. 2.

In the present study, the quilibrium flexibility of PVP chains are evaluated according to Eqns 1 and 2. From the values of K_{θ} , obtained by different extrapolation procedures [9], the values of unperturbed dimensions, $(\langle r_0^2 \rangle / M)^{1/2}$, were calculated from Eqn. 6 using $\Phi_0 = 2.5 \times 10^{23} \text{ mol}^{-1}$

$$K_{\theta} = \Phi_0 (\langle r_0^2 \rangle / M)^{3/2} \dots \dots \dots (6)$$

The procedures utilized here for deriving K_{θ} are Stockmayer-Fixman (S-F), Kurata-Stockmayer (K-S) and our procedures (A-S-F) and (A-K-S) for correcting S-F and K-S methods respectively. Another procedure, Kamide-Moore (KM), for deriving K_{θ} , is also considered here. The relevant references of these procedures are given in our previous article [9].

The calculated values of K_{θ} are subject to an absolute error arising from the uncertainty in the value assigned to Φ_0 . However, the values of $(\langle r_0^2 \rangle / M)^{1/2}$ obtained by using $\Phi_0 = 2.5 \times 10^{23} \text{ mol}^{-1}$ were employed to calculate the values of σ in conjunction with the value of 0.292 \AA for $(\langle r_0^2 \rangle / M)^{1/2}$, which was calculated via Eqn.2 for PVP. The later value agrees with the value of 0.292 \AA , given by Levy and Frank [24] and by Scholtan [25].

Values of σ are tabulated in Table 1 as well as the values of the characteristic ratio $(\langle r_0^2 \rangle / nl^2)$, C_{∞} . Another measure of the flexibility of polymer chains is the persistence length a_p , which is defined as the average projection of an infinitely long chain along the direction of its first link. The values of a_p were calculated according to Eqn.7 [26] and tabulated in Table 1.

$$a_p = l [(\langle r_0^2 \rangle / 2nl^2) + 1/2] \dots \dots \dots (7)$$

For (KM) procedure a unique value of K_{θ} , $74 \times 10^{-3} \text{ dm}^3 \text{ kg}^{-1}$, was obtained for all solvents used [9]. Consequently, the values of 2.28, 10.38 and 8.76 \AA for σ , C_{∞} and a_p respectively, were derived. The resultant values are in agreement with those reported by Tonelli [27] and Meza and Gargallo [18], where a values of C_{∞} , ranging between 5 and 11 were reported by them. The obtained value for σ , 2.28, is in good agreement with the value

Table 1: The Flexibility Parameters of PVP

Sol-vent	S-F			K-S			A-S-F			A-K-S		
	σ	C_{∞}	a_p	σ	C_{∞}	a_p	σ	C_{∞}	a_p	σ	C_{∞}	a_p
a	2.14	9.14	7.81	2.16	9.34	7.96	2.26	10.21	8.63	2.28	10.38	8.70
b	2.16	9.34	7.96	2.17	9.44	8.04	2.30	10.58	8.91	2.30	10.58	8.91
c	2.13	9.03	7.72	2.15	9.24	7.88	2.27	10.30	8.70	2.30	10.58	8.91
d	2.13	9.03	7.72	2.15	9.24	7.88	2.27	10.30	8.70	2.29	10.48	8.84
e	2.14	9.14	7.81	2.17	9.44	8.04	2.27	10.30	8.70	2.30	10.58	8.91
f	2.16	9.35	7.97	2.18	9.53	8.11	2.29	10.48	8.84	2.30	10.58	8.91
g	2.22	9.83	8.34	2.23	9.92	8.41	2.28	10.38	8.70	2.29	10.48	8.84
h	2.25	10.10	8.55	2.26	10.21	8.63	2.29	10.48	8.84	2.29	10.48	8.84
i	2.28	10.38	8.76	2.28	10.38	8.76	2.28	10.38	8.76	2.28	10.38	8.76
mean	2.18	9.48	7.10	2.19	9.64	7.22	2.28	10.38	8.75	2.29	10.50	8.85

Eizner et al.[29] have shown that all flexible molecules are almost impermeable. For the sake of testing this fact, the values of the effective length of PVP unit, b , and the effective hydrodynamic radius of the monomeric unit, r_0 , were determined from the viscosity data. The values of b were calculated from Eqn.9, given by Kirkwood and Riseman [30].

$$R_e = n^{1/2}b \dots \dots \dots (9)$$

where n is the degree of polymerization. Eizner et al.[29] have shown that the treatment of the experimental data leads to

$$r_0 = b/2 \dots \dots \dots (10)$$

The values of R_e, b and r_0 were calculated from Eqns 8,9 and 10, respectively, and tabulated in Table(2). It can be clearly seen that the value of R_e increases with increasing the molecular weight of the polymer in the particular solvent and with increasing the volume fraction of ACT, in the binary solvent, for the particular molecular weight up to ϕ (ACT) = 0.2. Increasing ϕ (ACT), more than 0.2, leads to a decrease in the solvation power and, hence, R_e . This situation is reflected in the dependence of the $[\eta]$ on the molecular weight of the polymer and the thermodynamic quality of the solvent.

The dependence of b on the molecular weight has been reported in the literature [31]. Satisfactory agreement is observed between the mean values obtained in the present study and the values of 0.5+0.13 nm, for the hydrodynamic diameter of PVP molecules given by Pavlov et al. [32]. The complete impermeability of PVP molecules is concluded since the value of r_0 increases from 0.31 in solvent i(θ -solvent) to 0.67 in solvent c which possesses the highest thermodynamic quality. This result is supported by the fact that the intrinsic viscosity of PVP in solvent c, where the cosolvency effect is observed, is higher than the intrinsic viscosity of PVP in solvent i(θ -solvent). This conclusion is similar to that of Eizner et al.[29] and indicated the impermeability of all flexible molecules.

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