

# Flory Fox Factor, Expansion Factor And Interpenetration Function for Poly (Vinyl) Pyrrolidone

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**Summary:** The two parameter theories, being based on Gaussian chain statistics require that when  $\alpha=1$ , the quantity  $\Psi$  and  $A_2$  should approach zero. However, the experimental behaviour is different and unexplainable in PVP-Methanol system. For low molecular weight i.e.  $M < 10^5$  in case of PVP, mutually consistent relationships for  $\Psi$  and  $\alpha$  based on two parameter theories cannot reproduce experimental results. It also fails to describe completely the experimental behaviour of short chains in good solvents.

## Introduction

In continuation to our previous published research work[1-5] we gathered some more information for Poly(Vinyl) Pyrrolidone fractions in methanol. We calculated Flory-Fox factor, Expansion factor and Interpenetration function, a dimensionless quantity giving an idea about interaction in dilute solutions of flexible high polymers.

## Results and Discussion:

### Flory-Fox Factor

We calculated the Flory-Fox factor  $\phi$ , from the relation.

$$[\eta] = 6^{3/2} \phi \langle Rg^2 \rangle^{3/2} / Mw$$

The results are given in table 1, and the ratio of  $\phi$  to  $\phi_\infty$  is logarithmically plotted against  $M_w$  in Figure 1. The value  $2.84 \times 10^{-21}$  dl/g was used here for  $\phi_\infty$ . For polystyrene Yamakawa *et al* [6] noted that

the ratio  $\phi/\phi_\infty$  is substantially constant at  $M_w$  higher than  $10^5$  but steeply increases as  $M_w$  decreases from  $10^5$ . In case of PVP we observed quite opposite behaviour in the low molecular weight region, i.e. the ratio  $\phi/\phi_\infty$  decreases with decrease in molecular weight, our results are in good agreement with the widely accepted notion i.e Gaussian Theory [7], that  $\phi$  should decrease with decreasing chain length because of the draining effect, i.e. the decrease in the hydrodynamic interaction in the polymer chain.

Table 1: Values of intrinsic viscosities and Flory-Fox factor, for polyvinyl pyrrolidone fractions at 303 K

Fraction	$M_w \times 10^{-4}$	$[\eta]$ dl/g	$\phi \times 10^{-21}$ dl/g	$\phi/\phi_\infty$
I	8.54	0.342	5.64	1.99
II	6.18	0.285	5.55	1.95
III	5.54	0.249	5.02	1.77
IV	3.32	0.188	4.95	1.74
V	2.80	0.168	4.85	1.71
VI	2.86	0.130	4.14	1.46
VII	1.18	0.085	3.58	1.26

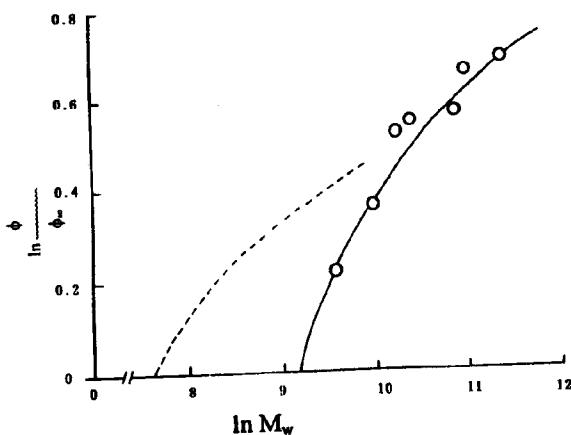


Fig. 1: Molecular weight dependence of the Flory-Fox factor,  $\phi$ , reduced with  $\phi_\infty$  for polyvinyl pyrrolidone in methanol at 30°C (o)=present data (....) the Gaussian theory values.

#### Expansion factor

The intrinsic viscosity can be related to the expansion factor  $\alpha$  and the root mean square unperturbed end to end distance  $(R^2\theta)^{1/2}$  by the Flory-Fox equation [8].

$$[\eta] = \phi [R^2\theta/M]^{3/2} M^{1/2} \alpha^3$$

The value of  $R^2\theta/M$  is characteristic of the given chain species and is a measure of chain flexibility. Usually it decreases slightly with increasing temperature. The magnitude of  $\alpha$  depends on solvent and temperature, through changes in the polymer-solvent interaction parameter  $\chi$ . The value  $(R^2/M)$  was obtained from the intercept of the plot of Stock Mayer-Fixman equation. The values of  $\alpha$  obtained are shown in table 2 at different temperatures. Values of  $\alpha$  are all larger than unity and increases very slightly with increase in temperature. Moreover, expansion factor also decreases with decrease in molecular weight in the low molecular weight range. The same trend was observed for PVA and PVP by Tadokoro *et al* [9].

Theory predicts that the expansion factor  $\alpha$  is a single valued function of "Z" [10]. The parameter "Z" should vary linearly with  $M^{1/2}$  but the proportionality constant cannot be determined by separate experiments. This has been the inherent difficulty in the data analysis and hence the source of great confusion.

Table 2 Expansion factor ( $\alpha$ ) values for polyvinyl pyrrolidone fractions in methanol at different temperatures (K)

Fractions	283	293	303	313	323
I	1.221	1.243	1.254	1.271	1.282
II	1.187	1.213	1.246	1.251	1.281
III	1.169	1.184	1.214	1.222	1.265
IV	1.147	1.171	1.202	1.207	1.238
V	1.142	1.160	1.192	1.200	1.224
VI	1.114	1.117	1.135	1.140	1.159
VII	1.092	1.106	1.096	1.098	1.098

For excluded volume, the combination of Yamakawa, and Shimada and Domb-Barrett [11,12] equations of flexible chain gives.

$$\alpha^2_s = [1 + 10Z^x + (70\pi/9 + 10/3)Z^x + 8\pi Z]^{2/5} \times [0.933 + 0.067 \exp(-0.85 Z^x - 1.39 Z^x)^2]$$

$$\text{Where } Z = (3/4) K (nk) Z$$

Where  $nk = \alpha$ ,  $Z^x = Z$ . If Z is increased indefinitely, the original DB equation gives  $\alpha^2 = 1.55 Z^{2/5}$  which is almost identical to the relation of Miyaki *et al* [13].

$$\alpha^2_s = 1.53 Z^{2/5}$$

Using this equation we have calculated the excluded volume "Z" for various fractions at different temperatures and the values are shown in Table 3. Once the excluded volume parameter is known then we can calculate the interpenetration function.

Table 3 Excluded volume parameter "Z" values for polyvinyl pyrrolidone fractions in methanol at different temperatures (K)

Fractions	283	293	303	313	323
I	0.937	1.025	1.071	1.017	1.196
II	0.814	0.907	1.037	1.058	1.191
III	0.754	0.804	0.911	0.941	1.046
IV	0.686	0.760	0.867	0.885	1.004
V	0.671	0.725	0.831	0.859	0.949
VI	0.593	0.601	0.651	0.665	0.722
VII	0.536	0.572	0.546	0.551	0.551

Interactions in dilute solutions of flexible polymers are usually discussed in terms of the interpenetration functions " $\Psi$ " [14]. This dimensionless quantity has been related by several approximate expressions to Osmotic second virial coefficient, excluded volume parameter "Z" and expansion factor ( $\alpha$ ). It is well known that excluded volume "Z" cannot be determined directly by experiments. However, the experimentally accessible expansion factor for the root mean square radius of gyration can

also be expressed as a function of "Z". Therefore, a plot of  $\Psi$  vs  $\alpha$  eliminates Z and provide a valuable test for the two parameter theories. Several theoretical approximations are available [15-17] for  $\alpha$  as a function of Z. Among those the treatment of Kurata *et al* [18], Yamakawa[19] and Yamakawa and Tanaka[20] give the relation.

$$\Psi = 0.547 [ 1 - (1 + 3.903 Z/\alpha^3) - 0.468 - A$$

This equation gives reasonable agreement with many experimental results [21] and that is why we preferred this to other combinations.

Apart from the numerical differences all but two of the approximate theories of  $\Psi$  yield monotonically increasing functions of Z. In the limit of high Z, they attain constant values. This behaviour has been confirmed only by experiments in which the excluded volume parameter Z ( $\alpha$ ) was varied by changing the temperature. In Figure 2 we present a plot of the  $\Psi$  parameter VS chain expansion factor for PVP-methanol system, along with theoretical predictions [22]. Moreover, according to equation (A) the limiting value is 0.547, which is significantly larger than experimental data, but more recent theoretical predictions, 0.231 by Ono and Freed [23] and 0.268 by Witten and Schafer [24] are in closer agreement with experiment.

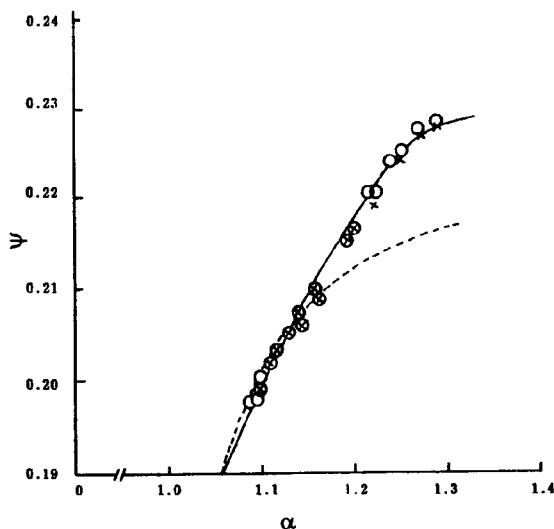


Fig. 2: Plot of  $\psi$  vs  $\alpha$  for polyvinyl pyrrolidone in methanol. All samples have mol.wet. lower than  $1 \times 10^5$  the dashed line represent the berry's theoretical line

In order to give a qualitative interpretation of the behaviour of  $\Psi$  we consider the molecular weight dependance of the second virial coefficient of PVP in methanol. If the molecular weight is lower than about  $10^4$ , the experimentally determined expansion factor " $\alpha$ " approaches unity [25]. The two parameter theories, being based on Gaussian chains, require that when  $\alpha = 1$ , the quantities  $\Psi$  and  $A_2$  should approach zero. However, the experimental behaviour is different and unexplainable.

The conclusion is that for low molecular weight i.e.  $M < 10^5$  in case of PVP, mutually consistent relationships for  $\Psi$  and  $\alpha$  based on two parameter theories cannot reproduce experimental results. Moreover, it also fails to describe completely the experimental behaviour of short chains in good solvents. However, a qualitatively correct interpretation is made possible if some third parameter is used. This behaviour can be explained qualitatively by taking into account the chain stiffness under good solvent conditions.

Table 4 Interpenetration function " $\Psi$ " values for polyvinyl pyrrolidone fractions in methanol at different temperatures (K)

Fractions	283	293	303	313	323
I	0.202	0.224	0.226	0.224	0.230
II	0.191	0.219	0.225	0.225	0.230
III	0.189	0.214	0.219	0.221	0.225
IV	0.208	0.212	0.217	0.218	0.223
V	0.207	0.210	0.216	0.217	0.221
VI	0.202	0.202	0.206	0.206	0.210
VII	0.198	0.200	0.198	0.199	0.199

## Experimental

Viscosities were measured in methanol using Ostwald's viscometer while Light Scattering technique which in addition to Mw, supplies data for thermodynamic quality of solvent;(Second virial coefficient A ); for higher Mw it also provide information about the dimension of the polymer (radius of gyration, Rg). The shape of the angular dependence of scattered light may indicate the presence of even a tiny quantity of aggregates or microgels.

However, the choice of solvent for measurements by light scattering is restricted by: a) in the given solvent polymer must possess a sufficiently high refractive index increment,  $dn/dc$ . b) solution must be molecular and stable in time and c) solution must not exhibit the poly electrolyte effect.

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