Part-1: Viscometric and Light Scattering Studies of Poly(Vinyl Pyrrolidone)

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Summary: Poly(vinyl pyrrolidone) (PVP) K-30 sample was subjected to fractionation using ethanol-petroleum ether system as solvent and non solvent, eight fractions were obtained and studied having molecular weight in the range $1.17x10^4$ to $9.30x10^4$. The corresponding limiting viscosity numbers of the various fractions were determined and the data relating to the methanolic system conform with the theory. A relation between intrinsic viscosity and weight average molecular weight is derived. The second virial coefficient A_2 for different fractions were calculated showing increase with decrease in molecular weight. Although this increase is not very pronounce. It was also concluded that methanol is as good solvent as water for PVP light scattering study.

Introduction

Poly (vinyl pyrrolidone) (PVP) is one of the important product [1] resulting from the Reppe techniques; it has many interesting properties from both physical and biological aspects. This extraordinary versatile acetylene derivative finds utility in dozens of applications across many industrial and consumer markets: Pharmaceuticals, agricultural chemicals adhesives, beverages, cosmetics, toiletries, detergents, fibers, textiles, lithography, photography, paper manufacture and processing, oil- well drilling and so on.

Many authors have discussed the characteristics of poly (vinyl pyrrolidone); especially the physico-chemical [2-5] properties. However little attention was given to the flow properties of this water-soluble polymer solution, despite of its importance. Keeping all these and molecular weight in view, it was desired to characterize the material by a procedure which measure the molecular weight directly rather than by the interpretation of viscosity data and for this purpose over-here light catering photometry has been used. Also an attempt was made to relate intrinsic viscosity with molecular weight for poly (vinyl pyrrolidone).

Results and Discussion

The intrinsic viscosity for different fractions in PVP methanol system were obtained by extrapolating plot of η_{sp}/C versus concentration to zero concentration and the values are listed in column II of Table 1. The intrinsic viscosity increases with increasing molecular weight. When molecular weight increases, the size of the macromolecule automatically increases which causes more internal resistance to flow. The high internal resistance will in turn give rise to high intrinsic viscosity. The same trend was observed in case of polystyrene [10].

Table 1:

Fraction	$[\eta]$dl/g 20 C methanol	$M_v x10^{-4}$	$M_w x10^{-4}$ 436 nm	$M_w 10^{-4}$ 546 nm	$A_2 x10^4$ 436 nm	$A_2 x10^4$ 546 nm
I	0.368	7.649	7.783	9.302	3.031	3.016
II	0.295	5.470	6.129	6.221	3.045	3.020
III	0.256	4.573	5.539	5.536	3.261	3.053
IV	0.192	3.020	3.321	3.317	3.266	2.971
V	0.171	2.568	2.785	2.815	3.267	3.056
VI	0.137	1.872	2.219	2.294	3.271	3.083
VII	0.096	1.131	1.176	1.185	3.295	3.125

Since there was some doubt [2] as to the validity of extrapolating the reduced viscosity to zero concentration to obtain the limiting viscosity number, the effect of dilution was investigated. Using all fractions no significant deviation from the straight line, η_{sp}/C vs conc. was found. The data are shown graphically in fig. 1 and there is no indication of irregular behaviour.

From the light scattering study, the value of Hc/τ for seven fractions are given in Table 2. In all cases the value of Hc/τ increases with increase in concentration. Gul et al [11] describe same trend in case of Natural rubber. This increase may not only

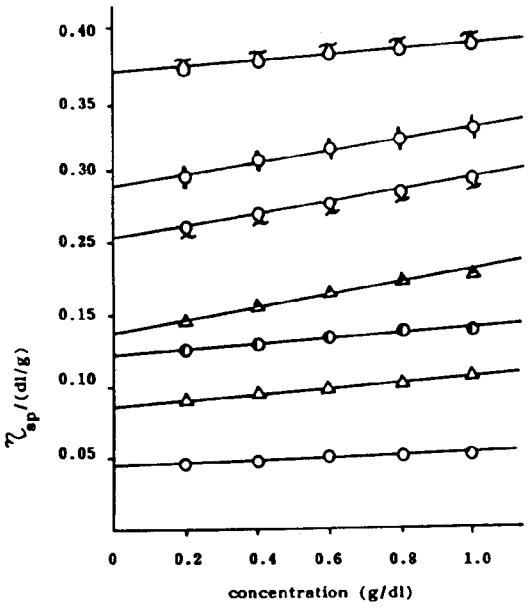

Fig. 1: plot of η_{sp}/C vs concentration for different PVP fractions at 20°C (Ō) = I, (◊) = II, (Q), = III, (▲) = IV, (●) = V, (Δ) = VI (O) = VII.

be due to the presence of separate macromolecules of PVP, but by their association and more complex supermolecular structure formation, size and degree of ordering of the macromolecules [12]. The weight average molecular weight M_w obtained from the inverse of the intercept of the plot of Hc/τ vs conc. at wavelengths 436 nm, and 546 nm are give in the column IV and V respectively in Table 1. It is observed that higher values obtained using longer wavelength confirms the results reported by Hengstenberg and Schuch [13].

Table 2: Values of Hc/τ x10^5 at 436 nm for various fraction at room temperature.

Conc (g/ml) 10^2	I	II	III	IV	V	VII	VIII
0.2	1.408	1.729	1.933	3.129	3.723	4.637	8.623
0.4	1.582	1.886	2.079	3.273	3.848	4.745	8.753
0.6	1.690	2.021	2.194	3.408	3.979	4.939	8.875
0.8	1.855	2.136	2.313	3.524	4.127	5,032	8.893
1.0	1.963	2.213	2.468	3.645	4.237	5.148	9.118

Column 6 and 7 of Table 1 lists the second virial coefficient A_2 at wavelength 436 nm and 546 nm respectively and its gradual change with variation of the molecular weight is interesting one. This gradual increase of A_2 with decreasing molecular weight is expected on theoretical grounds and has in fact been shown experimentally in polystyrene [14]. Although, the magnitude of the effect in case of PVP is rather small; $3.031x10^{-4}$ for M_w = $7.783x10^{-4}$, to $3.295x10^{-4}$ for M_w = $1.176x10^4$. (The fraction VIII has not been considered because it was obtained by evaporation of the residue rather than precipitation and showed a yellow color, which is due to the accumulation of impurities from all fractions). This small increase of A_2 may be due to the superimposition of structural effects on the normal dependence of A_2. These structural differences, e.g. degree of branching, could selectively affect the fraction procedure which is based on differential solubility and not solely on difference in molecular weight [15]. It was also reported that PVP in methanol fluoresces more strongly than does an aqueous solution of the same concentration and finally suggested aqueous solution of PVP for light scattering study, but our findings show that molecular weight obtained by light scattering using methanol as solvent is in excellent agreement with molecular weight obtained in water, so methanol is also equally good for PVP study.

The results of the viscosity and molecular weight determination obtained in PVP-methanol system are shown in fig.2 on a logarithmic scale.

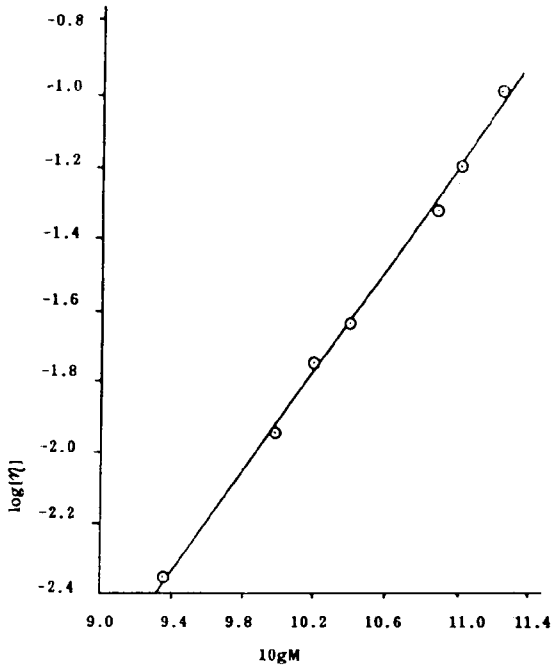

Fig.2: Intrinsic viscosity - weight average molecular weight plot for poly (vinyl pyrrolidone) in methanol at 20°C.

The slope of the line is equal to 0.70 representing "a" in the equation of Mark-Houwink-Sakurada:

$$[\eta] = KM^a$$

While the intercept is equal to 1.344×10^{-4} showing "K" value in the same equation. Frank and Levy [15] values for 'a" and "K" are 0.68 and 1.30×10^{-4} which are comparable to the values obtained by present work. The variation in the value of "a" is due to homogenity and molecular weight determination by unrefined techniques. Moreover, they did not apply any dissymmetry correction. The final M.H.S. equation we obtained for PVP K-30 sample is

$$[\eta] = 1.344 \times 10^{-4} M\ 0.70$$

The ratio of weight average and viscosity average molecular weight serves as an index of homogenity. Ideally sharp fractions have a ratio of 1.0. In Table 3, for each fraction the ratio is almost equal to 1.0 showing sharp fractions and thus the above suggested equation is valid for both number-average and weight- average molecular weight in the present case.

Table-3:

Fraction	Mw/Mv
I	0.985
II	1.081
III	1.168
IV	1.040
V	1.081
VI	1.195
VII	1.135

Scholtman [16] reported sudden bending of the molecular chain as the molecular weight increases, but in the present work no such bending was observed and the logarithmic relationship between $[\eta]$ and M_w in the entire range is linear on thus confirming the results of Ahmad et al [17].

Experimental

For this study PVP, K-30 sample was obtained from GAF corporation, Wayne N.J. The sample was subjected to fractional precipitation using ethanol-petroleum ether as solvent non solvent system in a accordance with techniques described elsewhere [6]. The starting material was

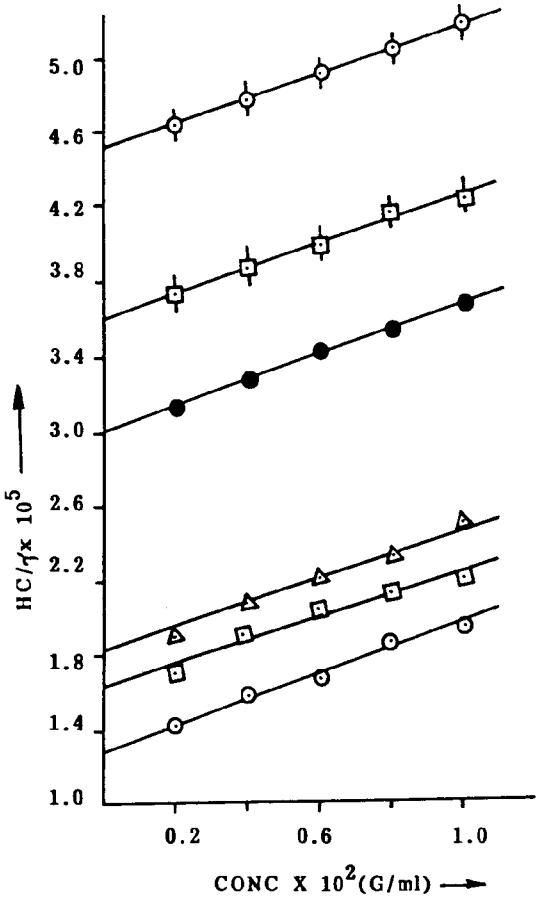

Fig.3: Plot of HC/t vs conc. for deferent PVP fraction at λ = 436 nm. (O) = I = II Δ = III (O) = IV = V (o) = VII

2.0% 500 ml solution. Each fraction was separated by dropwise addition of the non-solvent and thus eight fractions were separated, dried at 50°C and redissolved in anhydrous methanol for present study.

Limiting viscosity number

For this determination, a calibrated viscometer of negligible kinetic energy correction was used. The concentration range was from 0, 2-1.0g/dl and all the measurements were made at 293K ± 0.5 according to the Huggin's equation by plotting η_{sp}/C versus concentration and extrapolating to zero concentration, from the intercept, one get limiting viscosity number (intrinsic viscosity) being in dl/g.

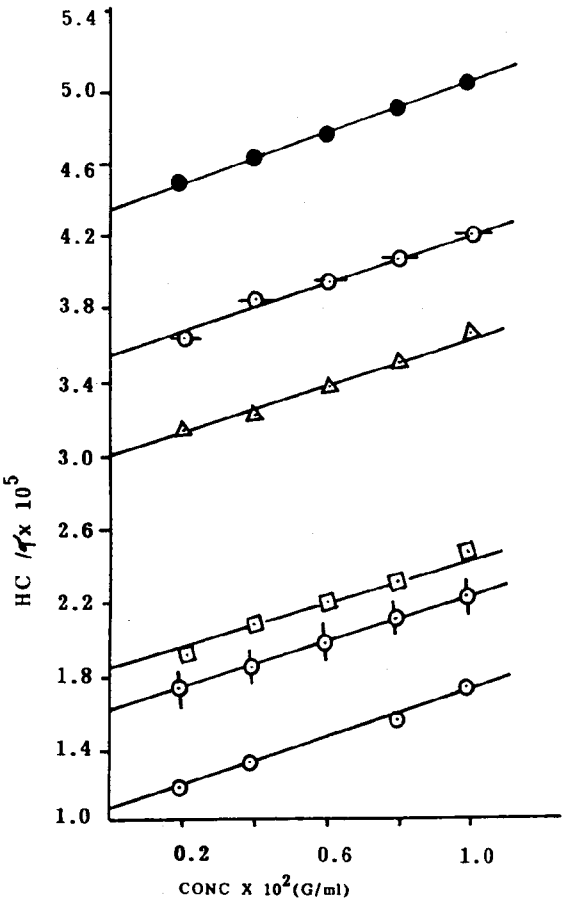

Fig.4: Plot of HC/t vs conc for different PVP fractions (o) = I (ϕ) = IIo= III Δ = IV (o) = V (•) = VII

Light scattering in methanol

The reading of the solvent and solutions of the same concentration used for viscosity measurements were taken in Brice-Phoenix Universal light scattering photometer using blue and green light of waveleneght 436 nm and 546 nm respectively. The procedure described by Brice, Nutting and Halwer [7] was used to correct for fluorescence, and the turbidity data obtained from the photometer readings for calculating the relation H_c/τ. These values were plotted against concentration (g/ml) and for various fractions, the weight average molecular weights (M_w) were obtained by linear extrapolation to C = O according to the equation:

$$H_c/\tau = 1/M_w + 2A_2C$$

where $H = 32\pi^2n^2 (dn/dc)^2/3 \lambda^4\pi N$, C is concentration in g/ml, τ is turbidity, M_w is weight average molecular weight, n is the refractive index of the solvent, dn/dc is refractive index increment of the solute, and λ is wavelength of the light used. A_2 is the second virial coefficient.

To check the calibration of the photometer, the Rayleight ratio for benzene was measured at 436 nm and found to be $4.18x10^{-5}$. This is 99.4 percent is agreement with the values reported by Brice-Halwer and Speiser [8] and 99.85 percent with the value reported by Oster [9].

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References

1. W. Reppe 1949. "Poly (Vinyl Pyrrolidone)", Verlag Chemie, Weinheim.
2. B. Jirgensons, *Macromol.Chem.*, **6**, 30 (1951).
3. H.P. Frank, B. Barkin and F.R. Eirch, *J.Am.Chem.Soc.*, **61**, 1357 (1959).
4. L.C. Cerny, T.E. Hetninik, and J.F.Meiner, *J.Polym.Sci.*, **44**, 539 (1960).
5. G. Oster, and E.H. Immargut, *J.Am.Chem.Soc.*, **76**, 1393 (1954).
6. N. Ahmad and B.Ahmad, *J.Chem.Soc.Pak.*, (accepted) (1990).
7. N. Brice Nutting and Halwer, *J.Am.Chem. Soc.*, **75**, 824 (1953).
8. H. Brice Halwer, and Speiser, *J. Opt. Soc. Am.* **40**, 768 (1950).
9. G. Oster, *Analyt Chem.*, **25**, 1165 (1953).
10. N. Ahmad, A.K. Bhettani and A. Rashad, *J.Chem.Soc.Pak.*, **12**(1), 62 (1990).
11. V.E. Gul, G.S. Klitenik, *Colloid Zhur* **16**, 171 (1954).
12. Amin-ur-Rehman, M.Phil thesis submitted to Univ. of Peshawar (1990).
13. Hangstenberg and Schuch, *Makromol. Chem.*, **7**, 236 (1952).
14. P. Outer, C.I. Earr, and B.H. Zimm, *J.Chem. Phys.*, **18**, 830 (1950).
15. H.P. Frank and G.B. Levy, *J.Polym.Sci.*, **10**, 371 (1952).
16. W. Scholtan, *Makromol.Chem.*, **7**, 209 (1952).
17. N. Ahmad and S. Ali, *British polym. J.*, **14**, 114 (1982).