Intrinsic Viscosity, Huggin's Constant and Unperturbed Chain Dimension of Polyvinylpyrrolidone

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Summary: A viscometric method was used to determine the molecular weight, root mean square end-to-end distance, radius of gyration and unperturbed chain dimension in aqueous solution of poly(vinyl pyrrolidone) at different temperatures. It was observed that $[\eta]$ decrease with rise in temperature but opposite trend was observed in case of K_H. Moreover, the values of K_H at all temperatures lie in the range of good solvent. Strong association of polymer molecules was observed in aq.PVP solution and molecular characteristics i.e. root mean square end-to-end distance, radius of gyration, molecular weight and unperturbed dimension show low values at high temperature and high values at low temperatures.

Introduction

Polyvinyl pyrrolidone(PVP) is a film-forming polymer which accounts for many of its uses. It also exhibits a high degree of compatibility with inorganic salt solutions, natural and synthetic resins, and other chemicals. Small amounts effectively stabilize emulsions, dispersions and suspensions. It also forms chemicals complexes of practical importance [1].

From the previous study [2] of polymer solutions on the thermodynamic properties, it has been found that the intrinsic viscosity $[\eta]$ (a measure for the size of the isolated molecules) and Huggins constant K_H (a measure for their natural interaction) are both influenced by changes of the solvent power and temperature. Besides theoretical interest, such measurements are also important for technical resons (polymer addition in motor oil recovery etc.). Stock *et al* [3,4] described conformational and thermodynamic properties of the macromolecules by two independent parameters and are related respectively to the unperturbed average dimensions and the excluded volume effect of a given polymer in a given environments. Advances in the preparation of stereoregular polymers have stimulated the need to characterize their microtacticity and fine structure [5,7]. Therefore, it is of considerable interest to derive information about the dimensions of macromolecules in the absence of both inter and intra-molecular interaction, such condition being obtained when a polymer is dissolved in Theta (θ) solvent. It is well known that Theta (θ) conditions are those at which the excluded volume effect and long range polymer-polymer interactions in a particular solvent compensate [8]. Under these conditions one obtains what is called "unperturbed" dimensions of the polymer chain.

The conventional method of determining the limiting viscosity number involves the use of one of viscosity-conc. relations for extrapolating to zero conc. Among the various viscosity-conc. relationships employed, the Huggin's equation:

$$\eta SP/C = [\eta] + K_H [\eta]^2 C \text{--- (A)}$$

respresents the experimental data quite accurately, particularly in the low concentration range.

Due to wide application of PVP, an extensive viscometric study was made to find the size, shape, radius of gyration and unperturbed dimension of PVP polymer molecule.

Experimental

The sample PVP, was obtained from E.Merck Co. (England), used as such without fractionation and further purification and was readily soluble in water at room temperature. The concentration range was from 0.4 g/dl to 2.0 g/dl with an interval of 0.4 g/dl. The viscosity of each solution was determined using Ostwald viscometer. The viscometer was calibrated and for each solution at least three flow times were noted.

In addition to the effect of concentration on viscosity, temperature was also taken into account. The range of temperature was 15-75°C with an interval of 10°C. The variation in temperature was less than ± 0.5°C.

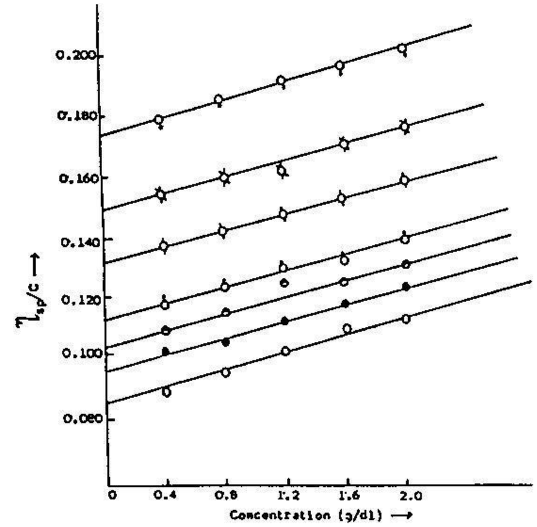


Fig.1: Plot η_{sp}/C vs concentration at different temperature for aqueous PVP solution (♀) = 15°C, (☿) = 25°C, (ϕ) = 35°C (Ȯ) = 45°C, (◒) = 55°C, (●) = 65°C, (O) = 75°C.

The mean square end-to-end distance was calculated by

$$[\eta] = \theta(R^2)^{3/2} / M \qquad (B)$$

and unperturbed dimension by

$$(R^2/M)^{1/2} = \frac{[[\eta]\, K_H]^{1/3} \times 10^{-7}}{2.87 \times M\, 1/2} \qquad (C)$$

Results and Discussion

The aim of the present work is to characterize and determine the size, shape, molecular weight and unperturbed dimension of the polymer molecules. Among different experimental techniques viscometric method was used due to its simplicity and high sensitivity to aggregation.

The viscosity of the polymer solution was measured at different temperature for different concentrations. From this data, the relative, specific and reduced viscosities were calculated and are given in Tables 1-3. It was observed that all types of viscosities increases with concentration and decreases with temperature. The increase in viscosity with concentration may be due to increase of interaction or frictional force among polymer-polymer or polymer-solvent molecules, but with rise in temperature these interactions decrease. Also, the lower the temperature, the more pronounced structure formation is and hence greater is the viscosity.

Table-1: Relative Viscosity of aq.PVP Solutions at Different Temperatures.

	CONCENTERATION				
Temp °C	0.4%	0.8%	1.2%	1.6%	2.0%
15	1.0727	1.1503	1.2305	1.3169	1.4079
25	1.0624	1.1281	1.1965	1.2752	1.3557
35	1.0559	1.1151	1.1775	1.2439	1.3199
45	1.0479	1.1006	1.1584	1.2142	1.2801
55	1.0447	1.0942	1.1530	1.2015	1.2521
65	1.0418	1.0861	1.1372	1.1917	1.2523
75	1.0365	1.0784	1.1251	1.1796	1.2318

Table-2: Specific Viscosity of aq. PVP solution at different temperatures.

	CONCENTRATION				
Temp °C	0.4%	0.8%	1.2%	1.6%	2.0%
15	0.0727	0.1503	0.2305	0.3169	0.4079
25	0.0624	0.1281	0.1965	0.2752	0.3557
35	0.0559	0.1151	0.1775	0.2439	0.3199
45	0.0479	0.1006	0.1584	0.2142	0.2801
55	0.0447	0.0942	0.1530	0.2015	0.2521
65	0.0418	0.0861	0.1372	0.1917	0.2523
75	0.0365	0.0784	0.1251	0.1796	0.2318

Table-3: Reduced viscosity (dl/g) of aq. PVP solutions at different temperatures

	CONCENTRATION				
Temp °C	0.4%	0.8%	1.2%	1.6%	2.0%
15	0.18175	0.18787	0.19210	0.19806	0.20390
25	0.15600	0.16012	0.16375	0.17200	0.17785
35	0.13975	0.14387	0.14790	0.15240	0.15995
45	0.11975	0.12575	0.13200	0.13387	0.14010
55	0.11175	0.11775	0.12750	0.12590	0.12605
65	0.10450	0.10760	0.11430	0.11980	0.12610
75	0.09125	0.09800	0.10425	0.11225	0.11565

The reduced viscosity is used to determine an important property, the intrinsic viscosity [η] which is related to the size and molecular weight of the polymer. The change of reduced viscosity with concentration is generally expressed according to well-known Huggin's equation (A) in which K_H is the Huggin's constant and can be taken as measure of interaction among polymer molecules. The values of $[\eta]$ and K_H at various temperature are given in Table-4. The $[\eta]$ decreases regularly with temperature due to hydrodynamic value and by the term α [9]. It may also be due to the fact that at lower temperature the polymer forms supermolecules and due to these bulky particles, rate of flow is small and hence the $[\eta]$ is large while at higher temperature these supermolecules break and due to less bulky particles, the rate of flow is large and hence the $[\eta]$ is small.

Table-4: Molecular Characteristics of aq PVP solution at different temperature.

Tempt °C	$[\eta]$ (dl/g)	K_H	Mv	$(\gamma^2)^{1/2}$ (cm)	$(S^2)^{1/2}$ (cm)	$(\gamma^2)^{1/2}$
15	0.172	0.4549	23646.77	9.43×10^{-7}	1.5716×10^{-7}	6.132×10^{-9}
25	0.150	0.6170	18438.15	7.55×10^{-10}	1.258×10^{-10}	5.560×10^{-12}
35	0.133	0.7708	-	-	-	--
45	0.115	0.8100	-	-	-	-
55	0.106	0.9530	-	-	-	-
65	0.0125	1.3000	-	-	-	-

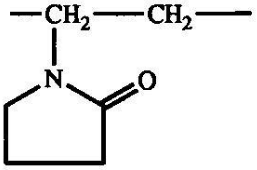
The increase in the value of K_H with temperature means that water acts as good solvent at lower temperature and its quality become worsens as temperature rise. Moreover the value of K_H lie in the range of good solvent [10].

The moleculear weight was calculated by Mark-Houwink-Sakurada equation

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

The "K" and "a" value for PVP in water at 25°C is 67.6×10^{-5} and 0.55 respectively [11]. The values of viscosity average molecular weight thus calculated are comparable with the literature values [12]. This molecular weight was used to calculate root mean square end-to-end distance, radius of gyration and unperturbed dimension and are listed in Table-4. As the values of "K" and "a" are known only at two temperatures, therefore, the values of molecular weight, unperturbed dimension, root mean square end-to-end distance and radius of gyration were calculated for 15 and 25°C.

The value of root mean squar and end-to-end distance is high at low temperature and low at high temperature showing high expansion at low temperature. Similarly the radius of gyration at the same temperature is lower than root mean square end-to-end distance suggest that there is higher length to width ratio indicating that polymer molecules are in the form of linear flexible chain [13]. The unperturbed chain dimension at low temperature may be due to the immobility of solvent molecules which become mobile at higher temperature hence perturbing polyer molecules. Moreover the ratio of $[\eta\ 65]$ to $[\eta\ 15]$ is less than 0.85 indicates that there exist strong association among the polymer molecules. This strong association in aq.PVP solution take place through H_2O molecules, and hydrogen bonding is responsible for it [14]. The structural unit of PVP provides a very good site for hydrogen bonding.



The high electronegativity of the oxygen atom on pyrrolidone ring attracts the hydrogen atoms of water molecules. (Dimerization, Trimerization or Oligomerization of water molecules). Hydrogen bonded to one PVP chain finally may acts as bridge connecting two PVP chains together. This picture of solvation of PVP by water is almost similar to the work of Jellinek *et al* [15] where they observed that water bound by PVP has a structure very close to that of ice. An ice like structure of water attached to PVP chains confirms the view that the extent of hydrogen bonding is quite high.

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