

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

INTRINSIC VISCOSITY OF AQUEOUS POLYVINYL ALCOHOL SOLUTIONS

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The behavior of polyvinyl alcohol aqueous solutions was investigated by viscometry. In region of very low polymer concentration, the reduced viscosity as a function of concentration deviates from linearity in the Huggins plots. The analysis of the concentration dependence of polymer solutions in terms of $\ln(\eta_{rel})$ vs. concentration provides the possibility to obtain accurately the intrinsic viscosity values. The relationship between the intrinsic viscosity and the molecular weight for polyvinyl alcohol in water at 30°C was examined and discussed.

INTRODUCTION

A parameter of great importance for polymer characterization is the intrinsic viscosity, $[\eta]$, which depends on the concentration and size of the dissolved macromolecules, as well as on the solvent quality and temperature. Usually, it is evaluated by extrapolation of experimental data to zero polymer concentration or, for fast evaluations, from measurements performed at a single concentration.

Despite a considerable number of theoretical and experimental studies (as for example several studies reported during last ten years¹⁻¹¹), the current understanding of the viscosity behavior of neutral polymer solutions at low concentrations is still far from being complete. Systematic errors appear in the evaluation of the intrinsic viscosity, being originated from the improper technique by which the viscosity of polymer solution is determined at very low concentrations. In some cases, below a definite concentration, the curves of reduced viscosity plotted against concentration show either an upward or a downward turn as a function of concentration. This can be due to the adsorption of the polymer chains on the glass wall

of the viscometer, but also to an expansion of the individual coils, conformational changes or others effects.¹¹ Yang *et al.*^{7,8} considered that the anomalous viscosity behavior of neutral polymer solutions at low concentrations can be avoided if the flow time of polymer solution at zero concentration is considered to determine the intrinsic viscosity instead of the measured flow time of the pure solvent. This is not valid for all polymer-solvent systems, our previous studies on polyacrylonitrile solutions in dimethylformamide^{1,11} showed that the turn of the η_{sp}/c curves could be due in part to the adsorption of polymer chains on the glass wall of the viscometer, but also in part to an expansion of the individual coils or conformational changes of macromolecules in solution. The adsorption of the polymer onto capillary wall surface usually occurs in the glass viscometer and determines a reduction of the capillary diameter, as well as a loss of polymer and a change of the equilibrium concentration in the viscometer.

Many efforts are continuously carried out in order to obtain a reliable equation for determining the intrinsic viscosity by using the viscometric data

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obtained at different concentrations. Recently,¹²⁻¹⁵ a new phenomenological approach was proposed as alternative method for the determination of the intrinsic viscosity for the polyelectrolytes, in presence and in the absence of salts. The value of the intrinsic viscosity is determined from the initial slope of the dependence of $\ln \eta_{\text{rel}}$ (where η_{rel} is the relative viscosity) as a function of concentration at sufficiently low shear rates and polymer concentrations. This method was also successfully applied to polyacrylonitrile solutions in dimethylformamide.¹⁶ In this study, we apply this concept to aqueous solutions of polyvinyl alcohol (PVA) with different molecular weights in order to calculate the intrinsic viscosity values and

then to determine the viscosity – molecular weight relationship.

RESULTS AND DISCUSSION

Intrinsic viscosity of PVA solutions

The intrinsic viscosity, $[\eta]$, can be evaluated from the viscosity measurements which provide data at finite concentration. The most general relationship between the intrinsic viscosity and dilute solution viscosity takes the form of power series in concentration (c):

$$\frac{\eta_{\text{sp}}}{c} = [\eta] + k_1 \cdot [\eta]^2 \cdot c + k_2 \cdot [\eta]^3 \cdot c^2 + k_3 \cdot [\eta]^4 \cdot c^3 + \dots \quad (1)$$

The $[\eta]$ values for a polymer solution can be obtained by using extrapolation methods to infinite dilution, such as Huggins equation:

$$\frac{\eta_{\text{sp}}}{c} = [\eta]_{\text{H}} + k_{\text{H}} \cdot [\eta]_{\text{H}}^2 \cdot c \quad (2)$$

k_{H} is referred to as the Huggins dimensionless constant and relates to the size and shape of polymer segments, as well as to hydrodynamic interactions between different segments of the same polymer chain; η_{sp} represents the specific viscosity ($\eta_{\text{sp}} = \eta_{\text{rel}} - 1$) which is the fractional change in viscosity produced by adding the solute and η_{rel} is the relative viscosity showing the change in viscosity, usually expressed as a ratio between the viscosity of the polymer solution and the viscosity of the pure solvent.

Figure 1 presents the viscometric dependences according to the method of Huggins obtained for PVA samples (Table 1) in water at 30°C. The values of $[\eta]_{\text{H}}$ and k_{H} obtained for PVA samples in the dilute regime (for which $1.2 < \eta_{\text{rel}} < 1.9$) are given in Table 1. It can be observed that k_{H} is higher than 0.5 for low molecular weight sample. This can be due to stronger polymer-polymer interactions in competition with polymer-solvent interactions. Also, in the region of low polymer concentrations (for which the values of the relative viscosity are less than 1.2) the reduced viscosity (η_{sp}/c) deviates from the linear dependence given by equation (2) and this made more difficult the correct evaluation of the intrinsic viscosity through the extrapolation to zero polymer concentration.

Table 1

Weight average molecular weights of PVA samples and the viscometric data obtained in water at 30°C, according to different approaches

Sample	$M \times 10^{-4}$ (g/mol)	% hydrolyzed	$[\eta]_{\text{H}}$ (dL/g)	k_{H} eq. (2)	$[\eta]_{\text{w}}$ (dL/g)	B	$[\eta]^*$ (dL/g)	k_{H} eq. (4)
1	0.95	80	0.238	0.688	0.235	0.022	0.233	0.478
2	4.05	98-99	0.495	0.270	0.498	0.264	0.265	0.236
3	6.50	98-99	0.543	0.357	0.592	0.235	0.452	0.265
4	8.49	98-99	0.741	0.483	0.785	0.217	0.521	0.283
5	16.60	98-99	1.154	0.432	1.182	0.175	0.726	0.325

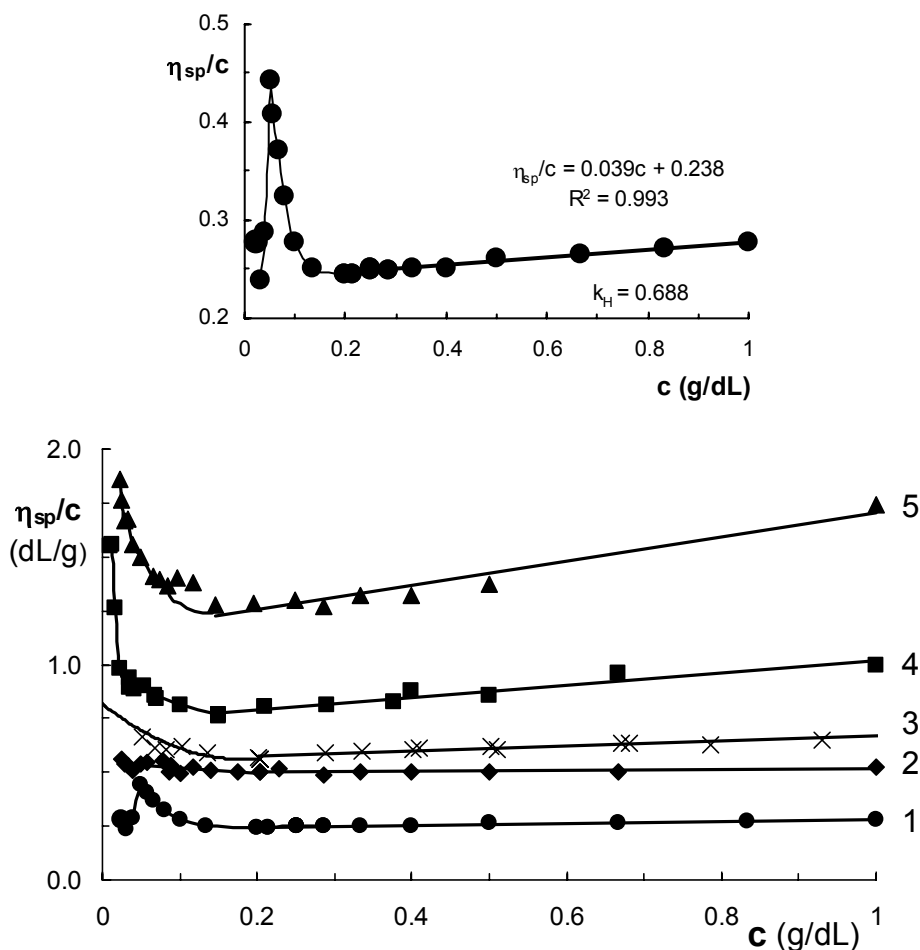


Fig. 1 – Dependence of the reduced viscosity as a function of concentration for solutions of PVA (samples 1-5, Table 1) in water at 30°C. The insert shows an enlargement of the plot obtained for sample 1.

Upward changes in the slope of η_{sp}/c as a function of concentration were reported for polyelectrolytes, due to the electrostatic repulsion between the charged groups of the macromolecules strongly increases upon dilution.¹⁷ Moreover, experimental results have showed that the dependences of η_{sp}/c versus polymer concentration reach a maximum, which in very dilute solutions is followed by a rapid decrease of the reduced viscosity.^{13,17} We depicted a such maximum for sample 1 (clearer evidenced in the insert from Figure 1), which can be explained as being due to the fact that in this point the polymer reach probably its final state of expansion in a finite domain of concentration. The reduced viscosity further decreases with the dilution. For sample 2 the maximum is less evidenced and for higher molecular weight samples probably this maximum can be reached for lower polymer concentrations and it is very difficult to find this experimentally.

Recently,¹²⁻¹⁵ a new alternative method was proposed for the determination of the intrinsic viscosity of polyelectrolytes in absence of salts, according to the following equation:

$$\ln \eta_{rel} = \frac{c[\eta]_w + Bc^2[\eta]_w[\eta]^*}{1 + Bc[\eta]_w} \quad (3)$$

where B represents a system specific constant and $[\eta]^*$ is the characteristic specific hydrodynamic volume.

We applied this method to neutral solutions, *i.e.*, polyacrylonitrile in dimethylformamide,¹⁶ and the results are close to those determined by applying the Huggins equation to the experimental data obtained in the dilute regime.

Figure 2 gives the concentration dependence of $\ln \eta_{rel}$ for PVA samples in water at 30°C. By modeling the viscometric dependences in terms of $\ln \eta_{rel}$ vs. concentration, the values of the intrinsic

viscosity ($[\eta]_w$) were evaluated, as well as the values of parameters B and $[\eta]^*$ (Table 1).

It can be observed that the values of the intrinsic viscosity determined by applying the equation (2) to the experimental data for which $1.2 < \eta_{rel} < 1.9$ are closed to those determined from the initial slope (eq. 3) (Table 1).

In order to discuss the hydrodynamic interactions, Wolf *et al.*¹⁵ deduced the following interrelation for the Huggins constant:

$$k_H = \frac{1}{2} - B \quad (4)$$

which only holds true for the range of pair interactions between the solute.^{15,18} The particular situation of $B = 0$ consequently translates to $k_H = 0.5$ (weak polymer-solvent interactions).

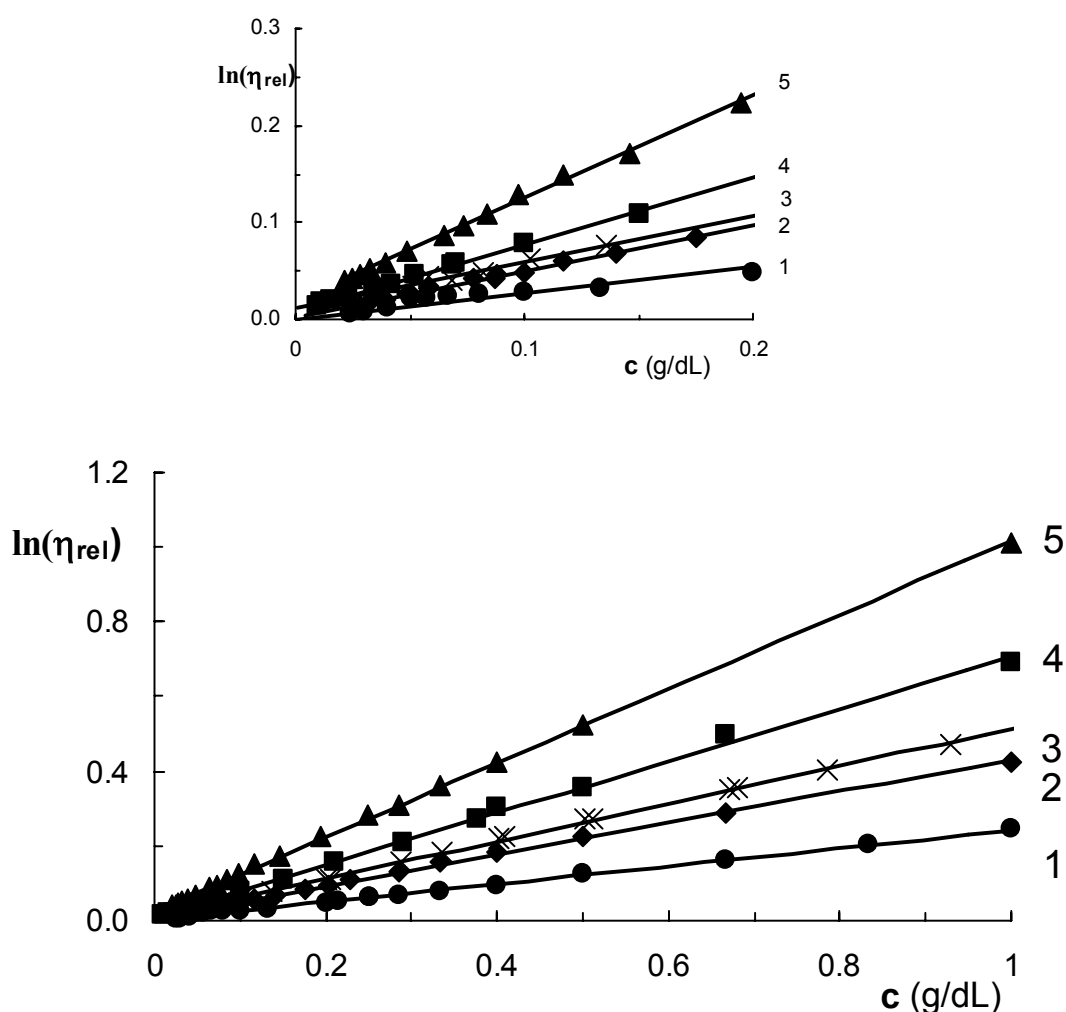


Fig. 2 – Plot of $\ln(\eta_{rel})$ as a function of concentration for PVA samples in water at 30°C.

The insert shows an enlargement of the plot for very low PVA concentrations.

The values of k_H calculated with the equation (4) are given in Table 1. The k_H value is close to 0.5 for sample 1, showing unfavorable polymer-solvent interactions for a sample 80% hydrolyzed, whereas for samples 2–4, having high degree of hydrolysis (98–99%) k_H presents values close to

0.3, suggesting favorable polymer-solvent interactions. Also, these values can be considered more realistic than those determined according to the equation of Huggins, because the last dependence becomes non-linear at very low polymer concentrations and the extrapolation procedure becomes inapplicable.

Mark-Howink relationship

The dependence of the intrinsic viscosity on the molecular weight (double logarithmic plot) for

PVA in water at 30°C is shown in Figure 3 and leads to the equation:

$$[\eta] = 1.38 \times 10^{-3} M^{0.56} \text{ (dL/g)} \quad (4)$$

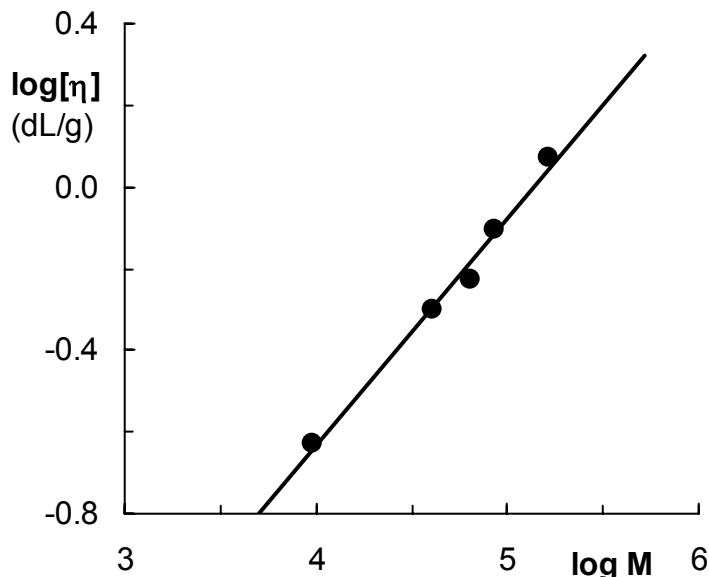


Fig. 3 – $[\eta]$ - M double logarithmic plot for PVA samples in water at 30°C.

For syndiotactic-rich PVA samples with molecular weight in the range 3.5×10^4 g/mol– 12.5×10^4 g/mol, literature¹⁹ gives the following dependence:

$$[\eta] = 0.734 \times 10^{-3} M^{0.63} \text{ (dL/g)} \quad (5)$$

The differences between our data and literature data can be due to the sample characteristics or the method used for the determination of $[\eta]$. Aqueous solutions of syndiotactic-rich PVA samples are very unstable; *i.e.*, below 80°C they become turbid, can form easily aggregates or gels.

PVA is known to dissolve more or less easily in water, due to the degree of hydrolysis of the poly(vinylacetate) precursor polymer. At high degree of hydrolysis (> 98%), PVA is highly crystalline and forms strong interchain hydrogen bonds, affecting its solubility in water.²⁰ Thus, a solubilization temperature higher than 80°C is required to dissolve PVA completely. Upon cooling at 30°C, PVA remains in solution, but its storage time at this temperature does not exceed 2 days to avoid the formation of aggregates.

The effect of the association is influenced by the flow-induced crystallization of PVA solutions and by the thermal history in the preparation of the solutions.^{19, 20} Such solution does not form fibrous

precipitate in capillary viscometer if the flow is made at sufficiently low shear rate. In our measurements, for a given sample, changes of the solution viscosity in time were found negligible and all samples remained homogeneous during the experimental investigations. Rheological measurements carried out at 30°C did not evidence flow-induced crystallization of PVA solutions.

EXPERIMENTAL PART

Four polyvinyl alcohol samples (denoted 1, 2, 4 and 5, Table 1) were purchased from Aldrich and a PVA sample (sample 3, Table 1) was provided from Loba Chemie.

Homogeneous PVA solutions were prepared by heating the PVA and water mixture at 80°C, waiting 2 days for reaching the thermodynamic equilibrium.

The viscometric measurements were carried out at 30°C with an Ubbelohde suspended-level viscometer. The flow time for the solvent was 156.74 s and the kinetic energy corrections were found to be negligible. The flow volume of the viscometer was greater than 5 mL, making drainage errors unimportant. In order to avoid any aging effects of PVA solutions, flow time measurements have been made on fresh solutions in less than 48 h. All the solutions and solvents were filtered through 0.45 μ m pore size membranes before being introduced in the viscometer. The solutions were prepared starting from an initial stock solution successively diluted in the viscometer. Each run time was repeated five times to give flow time measurements with an accuracy of 0.05 s.

CONCLUSIONS

In aqueous solutions, there are two possible intermolecular interactions among PVA chains or between PVA and water which can determine the association or aggregation: H-bonding between hydroxyl groups on PVA chains and H-bonding between the –OH groups of PVA and water molecules. The competition between these types of interactions will influence the properties of PVA solutions.

The analysis of the concentration dependence of $\ln(\eta_{rel})$, according to a new method proposed by Wolf,¹² instead of the traditional Huggins plots or similar evaluations, provides a general facility to obtain intrinsic viscosity. This method was verified for aqueous solutions of polyelectrolytes in the absence/presence of salt and we demonstrated its validity for solutions of non-ionic polymers in organic solvents. The intrinsic viscosity values can be determined more accurately by modeling the viscometric data in the region of very low concentrations according to this new procedure instead of the Huggins one.

The viscosity – molecular weight relationship was determined for PVA in water at 30°C, showing some differences as compared with literature data. Thus, a Mark-Houwink exponent of 0.56 was obtained in the present study, showing less favorable PVA-water interactions. Previously,¹⁹ a value of 0.63 was reported for this parameter. These differences can be due to the both sample characteristics and the method used for the determination of the intrinsic viscosity.

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