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Viscosity study of the solutions of polyvinyl pyrrolidone in polar solvent

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ABSTRACT

Viscometric methods play a dominant role in studying the Polymer-Solvent interaction. Due to this interaction, there is an increase in viscosity of polymer solution over that of pure solvent. The intrinsic viscosity is the limiting value of the reduced viscosity at infinite dilution. The intrinsic viscosity has been used to study the extent of interaction between polymer and the solvent. In the present work, the intrinsic viscosity obtained through adiabatic compressibility and viscosity data is applied to the solution of Poly Vinyl Pyrrolidone in polar solvent at 308 K, 313 K & 318 K. Viscosity of the solvated part (η_s) is computed and its variation with molar concentration (n_2) is studied. The molar solvated volume (Φ_s) obtained from η_s is compared with the values of Φ_s computed using the traditional equation. The Huggin's coefficients A_η and B_η are determined from Viscosity study and compared with those obtained from solvation study.

Introduction

When a polymer is dissolved in a solvent, there is increase in viscosity over that of pure solvent. This is due to the interaction between the polymer and the solvent. Flory and Fox [1] suggested that the viscosity of polymer solution should depend on the volume occupied by the polymer molecules. As the concentration of polymer in solution increases, the Viscosity is governed by the intermolecular interaction of increasing order, which are connected with the overlapping of polymer molecules [2].The structure of the polymer molecule is represented by a highly entangled solid net, which is formed by the interaction of swollen macromolecular coils. The formation of such a net is caused by the energetic interaction between the polymer and the solvent. It is possible to get an idea about the solvent structure from the measurement of solution viscosity.

To express the Viscosity as a function of concentration, Polynomial relations have been suggested by Several investigators [3,4]. The coefficients A_η and B_η of the polynomials are regarded as a measure of the polymer-solvent interaction and polymer-polymer interactions respectively. Intrinsic Viscosity, which is given by $[\eta]$ or A_η, directly depends on the size and shape of individual polymer molecules in solution. Hence the knowledge of $[\eta]$ and its variation with temperature has been used for describing the extend of interaction between a polymer and the solvent.

Kalyanasundaram etal[5,6] have assumed that the viscosity of the polymer solution is the sum of the viscosity of the free solvent part and the viscosity of the solvated part similar to adiabatic compressibility and volume of the solution. On this basis, they have derived the expression for the viscosity of the solvated part (η_s). This expression is used for the solution of Poly Vinyl Pyrrolidone in polar solvent. The intrinsic viscosity is determined from Viscosity study and compared with the same obtained from solvation study.

Experimental:

The solutions of Poly Vinyl Pyrrolidone of concentration range from 0% w to 3% w were prepared by dissolving known quantities of PVP10 of molecular weight 10,000 (Sigma Aldrich Chemical Pvt.Ltd., Bangalore) in polar solvent namely propanol . Ultrasonic velocities of the solutions were measured using a fixed frequency continuous wave ultrasonic interferometer (Model F80, Mittal Enterprises, New Delhi) to an accuracy of ± 0.1 at a frequency of 2 MHz at 308 K, 313K & 318K. The temperature of the samples was maintained constant to an accuracy of ± 0.1° using a thermostatically controlled water bath. Density was measured using 10 ml specific gravity bottle at all above temperatures. The viscosity was measured using Ostwald's viscometer to an accuracy of ± 0.2% .

Viscosity of solvated part and molar solvated volume

The adiabatic compressibility of the solution is given as

$$\beta = (n_1 - n_2 S)\,\beta_0 /N \qquad \ldots\ldots\ldots (1)$$

Where n_1 is the number of solvent molecules present in the solution of molar concentration n_2, N is the number of molecules presents in the pure solvent, S is the molar solvation number and β_0 is the adiabatic compressibility of pure solvent.

The volume of the solution is written as

$$V = (n_1 - n_2 S)V_1 + n_2\Phi_s \qquad \ldots\ldots\ldots\ (2)$$

Where V_1 is the molar volume and Φ_s is the molar solvated volume.

Like adiabatic compressibility and volume, the viscosity of the solution is assumed to be the sum of viscosity of the free solvent part and the viscosity of the solvated part. Then,

$$\eta = [(n_1 - n_2 S)\eta_0/N] + n_2\eta_s \qquad \ldots\ldots (3)$$

where η_0 is the viscosity of the pure solvent and η_s is the viscosity of the solvated part.

In the light of equation (1), equation (3) is rewritten as

$$\eta = (\beta/\beta_0)\,\eta_0 + n_2\,\eta_s \qquad ----(4)$$

Thus,

$$\eta_s = (\eta\beta_0 - \eta_0\beta)/n_2\beta_0 \qquad -----(5)$$

The molar solvated volume Φ_s is obtained from η_s by substituting the value of $(n_1 - n_2 S)$ from equation (2) in equation (3) where $NV_1 = V$ for dilute solutions as

$$\Phi_s = (V/n_2)[1-(\eta/\eta_0) + n_2(\eta_s/\eta_0)] \qquad ------(6)$$

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φ_s is usually computed using the adiabatic compressibility data through the relation

$\Phi_s = (V/n_2)(\beta_0-\beta)/\beta_0$ -------(7)

Intrinsic Viscosity from the Viscosity of solvated part

Huggin's polynomial relation for the variation of viscosity with the concentration is

$\eta/\eta_0 = 1 + A_\eta n_2 + B_\eta n_2^2$

Rearranging the equation,

$[(\eta/\eta_0)-1]/n_2 = A_\eta + B_\eta n_2$ ---(8)

Since Φs varies linearly with n_2 we can write,

$\Phi_s = \Phi_{so} + S_s n_2$ ---------(9)

Assuming η_s to vary linearly with n_2 like Φ_s, we have,

$\eta_s = \eta_{so} + S_\eta n_2$ ---- (10)

where η_{so} is the viscosity of the solvated part at infinite dilution and S_η is the slope of the plot of η_s vs n_2.

From equation (6),

$[(\eta/\eta_0)-1]/n_2 = [\eta_s/\eta_0] - [\Phi_s/V]$ ----(11)

Sustituting the values of Φs and η_s from equations (9) and (10) in equation (11) we get

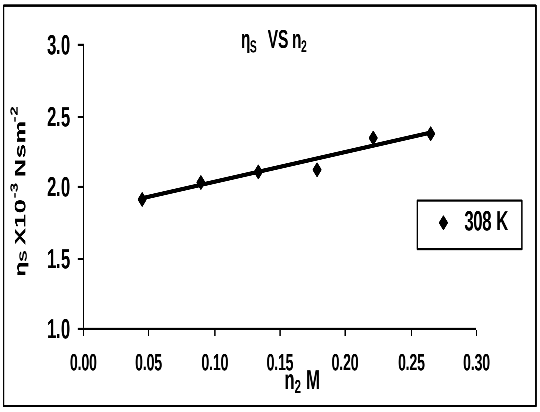
$$[(\eta/\eta_0)-1]/n_2 = [(\eta_{so} + S_\eta n_2)/\eta_0] - [(\Phi_{so} + S_s n_2)/V] \quad \text{----(12)}$$

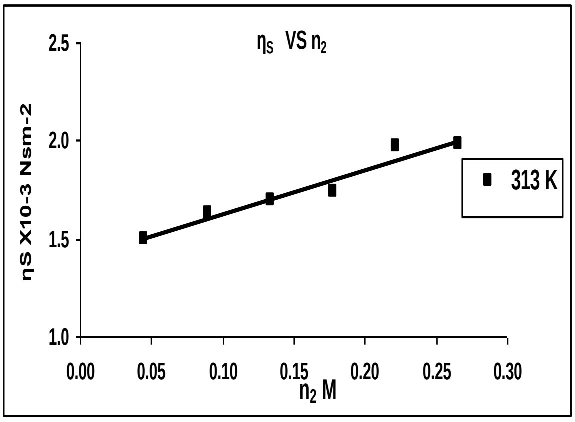
Comparing the coefficients of equations (8) and (12),

$A_\eta = (\eta_{so}/\eta_0) - (\varphi_{so}/V)$ ------ (13)

$B_\eta = (S_\eta/\eta_0) - (S_s/V)$ ------- (14)

Fig 1





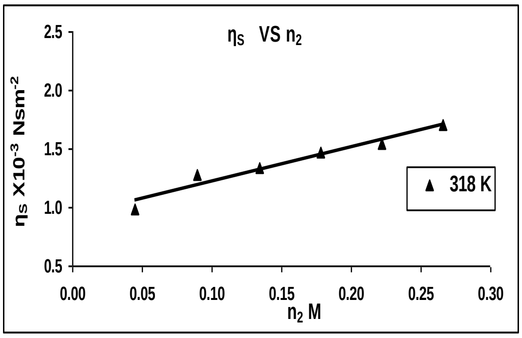
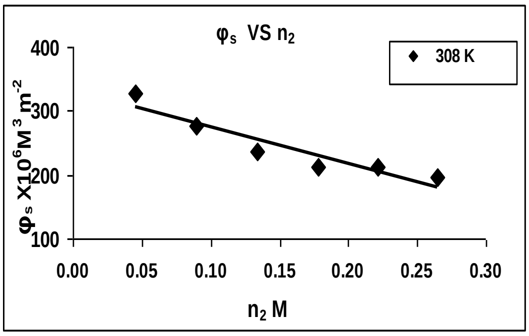
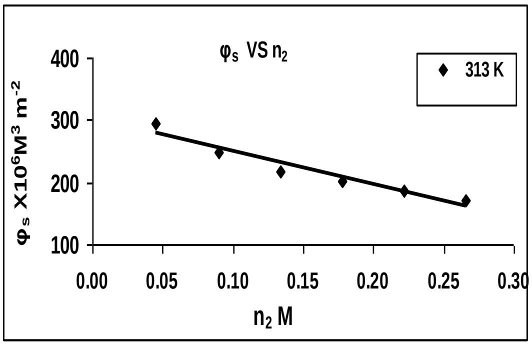


Fig 2





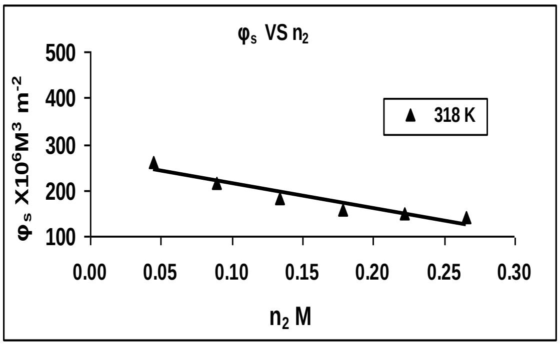
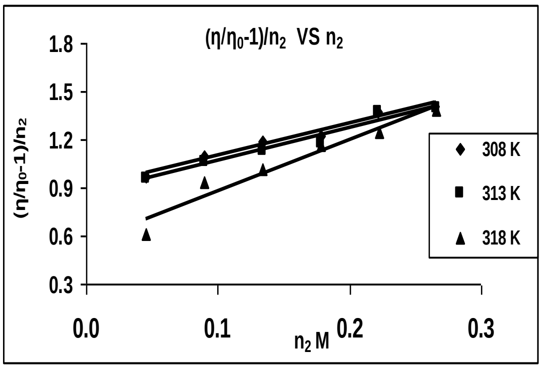


Fig 3



Results and Discussion:

The values of the viscosity of the solvated part ηs computed for different concentrations of PVP+ Propanol solution at 308K, 313K & 318 K are presented in Table (1). The molar solvated volume Φ_s computed from η_s equation (6) and using the adiabatic compressibility equation(7)are presented in Table (1). There is a good agreement between the two values reported.

The variation of viscosity of the solvated part with concentration is shown in [Fig 1]. The molar solvated volume Φ_s is found to vary linearly with concentration like η_s [Fig 2].From these two graphs, the constants Ss, S_η, Φ_{so} and η_{so} are found out. The intrinsic viscosity [η] or A_η and B_η are computed from these constants using equations (13) and (14) and are presented in Table (2). The plot of $(\eta/\eta_0 -1)/ n_2$ VS n_2 is shown for the temperatures 308K, 313 K and 318 K in [Fig 3]. This plot gives the Huggin's coefficients A_η and Bη which are also presented in table (2). There is an agreement between the values of Huggin's coefficients A_η and B_η obtained through these methods. This confirms the validity of the methodology applied.

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Table 1 Values of n_2, U, β, η, η_s and Φ_s for PVP + Propanol solution

Temp	n_2 M	U ms^{-1}	$\beta x10^{11}$ Nm^{-2}	η $x10^3$ NSm^{-2}	η_s $x10^3$ NSm^{-2}	$\Phi_s x10^6$ m^3M^{-1}	
						From Eqn 6	From Eqn7
308K	0.000	1116	104.0	1.478	-	-	-
	0.045	1122	102.4	1.542	1.908	327.9	327.9
	0.089	1126	101.4	1.623	2.035	277.6	277.6
	0. 134	1128	100.7	1.713	2.104	236.9	236.9
	0.178	1130	100.0	1.799	2.118	213.5	213.5
	0.221	1134	99.1	1.927	2.343	213.3	213.3
	0.265	1135	98.6	2.029	2.367	195.5	195.5
313K	0.000	1102	107.6	1.276	-	-	-
	0.045	1107	106.2	1.330	1.494	293.3	293.3
	0.089	1110	105.2	1.397	1.626	247.6	247.6
	0. 134	1112	104.5	1.469	1.693	218.0	218.0
	0.178	1114	103.7	1.542	1.734	202.8	202.8
	0.221	1115	103.2	1.664	1.966	185.9	185.9
	0.265	1116	102.7	1.747	1.981	171.5	171.5
318 K	0.000	1085	111.7	1.111	-	-	-
	0.045	1089	110.4	1.142	0.981	260.5	260.5
	0.089	1091	109.5	1.205	1.286	214.9	214.9
	0. 134	1092	108.9	1.263	1.334	182.2	182.2
	0.178	1092	108.5	1.342	1.471	157.5	157.5
	0.221	1093	107.9	1.418	1.550	150.4	150.4
	0.265	1094	107.5	1.521	1.703	140.9	140.9

Table 2 Values of η_{so}, S_η , Φ_{so} , S_s, A $_\eta$ and B $_\eta$ for PVP + Propanol solution

Temp	η_{so} $x10^3$ $NSm^{-2}M^{-1}$	S_η $x10^3$ $NSm^{-2}M^{-1}$	S_s $x10^6$ m^3M^{-2}	Φ_{so} $x10^6$ m^3M^{-1}	A $_\eta$		B $_\eta$	
					From graph	From eqn13	From graph	From eqn14
308 K	1.8195	2.101	-571.05	332.86	0.90	0.90	1.99	1.99
313 K	1.3962	2.2659	-524.72	301.5	0.86	0.80	2.10	2.30
318 K	0.9293	2.9432	-529.32	266.79	0.56	0.57	3.20	3.20