

Effect of solvent quality on the Viscosity of Dilute Solutions of PVC

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Summary: The dilute solution properties of two Poly(vinyl chloride) i.e., PVC samples of molecular weight 200,000 and 100,000 were studied viscometrically in four solvents. The effect of the nature of the solvent was determined showing the solvent power for PVC to be cyclohexanone > tetrahydrofuran > cyclopentanone > dioxane on the basis of $[\eta]$ and K_H . Hydrodynamic volume values are also reported for these PVC-solvent system and a similar order of solvent power is suggested. Unperturbed chain dimensions for PVC were determined by using Deb and Chatterjee equation for non-theta solvents and the values are discussed.

Introduction

Solution properties of polymer in the region of extreme dilution are of great importance both theoretically and experimentally. Solvent plays an important role in these properties. Solvent quality is important practically for both processing of polymer and during the service of the article made from them. The effect of the nature of solvent on the viscosity of a polymer solution is very much pronounced showing interaction of polymer with the solvent molecule. Poly(vinyl chloride) is industrially important polymer finding its use in every aspect of life, shown by the fact that its production is increasing every year and it has reached to 10.88 billions of Pounds [1-2]. Previously a number of studies of the interaction of poly(vinyl chloride) with solvent have been made

but there seems to have been a few systematic studies of the dilute solution properties with solvents [3-7]. Furthermore, all these studies are restricted to one or two temperatures. Hydrodynamic volume is another parameter which needs attention and has not given in the literature for PVC. Present study has been undertaken to find out all of these problems relating interaction of PVC with solvent under various conditions of temperature and molecular weight. An attempt has also been made to discuss the hydrodynamic volume with respect to solvent temperature and molecular weight.

The unperturbed chain dimension values of polymer in a given solvent are characteristic of the

given species and chain flexibility and are related to the viscosity of the polymer solution. In usual practice information about the unperturbed chain dimension of the macromolecule is derived in the absence of both inter- and intramolecular interaction. Such conditions being obtained when a polymer is dissolved in a theta solvent. However, as an ideal solvent is not always readily available, the unperturbed chain dimension may be calculated from measurement in non-ideal solvents using Deb and Chatterjee equation [8].

$$\left(\frac{r_o^2}{M_w}\right)^{1/2} = \left[\frac{[\eta]K}{(2.84)M_w^{1/2}}\right]^{1/3} \cdot 10^7 \dots\dots\dots(1)$$

Where $(r_o^2/M_w)^{1/2}$ = Unperturbed Chain Dimension and

M_w = Molecular weight.

$[\eta]_K$ is obtained from the plot of $1/[\eta]$ vs K_H . Intrinsic viscosity $[\eta]$ and Huggin's coefficient K_H were calculated using equation 2.

Results and Discussion

The values of $[\eta]$ and K_H serve as a measure of the solvent power. The use of $[\eta]$ in this way assumes that better the solvent thermodynamically, more extended will be the chain so that the hydrodynamic volume and, therefore, the $[\eta]$ will increase with increasing solvent power [11]. K_H has been used as a measure of the solvent power in the sense that smaller its value better the solvent [12]. The order of the solvent power obtained by the use of these different criteria for PVC samples (M_w , 100,000) is shown to be in the order CHO > THF > CPO > Diox. Furthermore values of K_H suggest that CHO, THF, and CPO are good solvents for PVC while DIOX, is a poor solvent. For the second sample of PVC (M_w , 200,000) K_H values give the same order of the solvent power as for the sample (M_w , 100,000). However, the $[\eta]$ values suggest that THF is better solvent than CHO. Since THF solutions were not heated at 80°C before use, the presence of aggregates might have led to higher values of $[\eta]$ than would be obtained if the polymer was molecularly dispersed. Alternatively solvation effect may have led to a large values of $[\eta]$. PVC is believed to be solvated

in solutions because of specific interaction between acid hydrogen atom of the polymer and basic solvent group. The combined and overall order of the solvent power on the basis of $[\eta]$ and K_H is thus CHO > THF > CPO > DIOX.

It can be seen from Table-1 and 2 that $[\eta]$ is decreasing with increasing temperature *i.e.* all the solutions are weakly exothermal. The type of critical solution temperature effects the temperature coefficient of the intrinsic viscosity [13]. In systems with upper critical solution temperature (UCST) the molecular coil swells more as temperature rises, leading to an increase in $[\eta]$ while in systems with lower critical solution temperature (LCST) it swells less, which lowers solvent quality. The value of $[\eta]$, therefore, falls with rise in temperature. In all the cases which we studied it is seen that $[\eta]$ decreases with temperature which means that all the solutions are following (LCST) phenomena. Furthermore we can explain the decrease in $[\eta]$ with increasing temperature by the fact that all these solvents are more or less polar.

Table-1: Intrinsic viscosity $[\eta]$ and Huggins coefficient K_H for PVC (M_w , 100,000) in various solvents.

System	$[\eta]$ (dl/g)	K_H	$[\eta]$ (dl/g)	K_H
	20°C		30°C	
CHO/PVC	0.8876	0.27	0.8504	0.28
THF/PVC	0.8705	0.30	0.8151	0.35
CPO/PVC	0.7818	0.40	0.7633	0.40
Diox/PVC	0.5393	0.78	0.5337	0.80
	40°C		50°C	
CHO/PVC	0.8029	0.27	0.7703	0.28
THF/PVC	0.7761	0.37	0.7426	0.37
CPO/PVC	0.7343	0.40	0.7043	0.41
Diox/PVC	0.5259	0.81	0.5245	0.74
	60°C		70°C	
CHO/PVC	0.7125	0.37	-	-
CPO/PVC	0.6833	0.43	0.6663	0.42
Diox/PVC	0.5218	0.79	0.4981	0.74

Hydrodynamic volume

When polymer is dissolved in a solvent it swells up due to solvation. Volume being occupied by the expanded coil along with the bound solvent is called hydrodynamic volume. Hydrodynamic volume (V_{hyd}) of the polymer molecules were calculated using the following relationship [14]

$$V_{hyd} = \frac{[\eta]M_w}{0.025N_A} \dots\dots\dots(3)$$

Table-2: Intrinsic viscosity $[\eta]$ and Huggins coefficients K_H for PVC (Mw. 200,000) in various solvents.

System	$[\eta]$ (dl/g)	K_H	$[\eta]$ (dl/g)	K_H
	20°C		30°C	
CHO/PVC	1.0898	0.31	1.0442	0.36
THF/PVC	2.2183	0.33	2.1057	0.36
CPO/PVC	0.8184	0.76	0.7735	0.77
Diox/PVC	—	1.26	0.6226	1.35
	40°C		50°C	
CHO/PVC	1.0129	0.37	0.9828	0.38
THF/PVC	2.0172	0.36	1.8739	0.43
CPO/PVC	0.7735	0.77	0.7343	0.85
Diox/PVC	0.6226	1.21	—	1.21
	80°C		70°C	
CHO/PVC	0.9598	0.39	0.9054	0.43
CPO/PVC	0.6869	0.96	0.6541	—
Diox/PVC	0.5990	1.21	0.5755	1.27

where $[\eta]$ = Intrinsic viscosity in dl/g, N_A is the Avogadro number and M_w is the weight average molecular weight of the polymer.

Values of the hydrodynamic volume of both samples of PVC are summarized in the Table-3 and Table-4.

Table-3: Values of hydrodynamic volume (V_h E18 cm³) of PVC (Mw, 100,000) in different solvents and at different temperatures.

t, °C	CHO	THF	CPO	Diox
20	5.8977	5.7841	5.1947	3.5934
30	5.6505	5.4159	5.0718	3.5462
40	5.3349	5.1568	4.8791	3.4944
50	5.1183	4.9342	4.6797	3.4983
60	4.7342	—	4.5402	3.4671
70	—	—	4.4272	3.3096

Table-4: Values of hydrodynamic volume (V_h E18 cm³) of PVC (Mw. 200,000) in different solvents and at different temperatures.

t, °C	CHO	THF	CPO	Diox
20	14.4824	29.4791	10.8757	—
30	13.8764	27.9827	10.5847	8.2910
40	13.4605	26.8066	10.2791	0.2738
50	13.0605	24.9023	9.7581	—
60	12.7548	—	9.1282	7.9601
70	12.0319	—	8.6924	7.6478

Hydrodynamic volume is a function of quality of the solvent and temperature. Better the quality of the solvent more strong will be the polymer-solvent interaction and hence more expanded will be the polymer coil. The values of

Table-5: Values of $1/[\eta]$, $[\eta]_K$ and $(r_o^2/Mw)^{1/2}$ of PVC (Mw=100,000) in different solvents and at different temperatures.

t, °C	Solvent	$1/[\eta]$	$[\eta]_K$	$(r_o^2/Mw)^{1/2}$ E9
20	CHO	1.1266		
	THF	1.1488	1.315	1.6610
	CPO	1.2791		
30	CHO	1.1759		
	THF	1.2268	1.1494	1.5880
	CPO	1.3101		
40	CHO	1.2456		
	THF	1.2885	0.9709	1.5012
	CPO	1.3610		
50	CHO	1.2982		
	THF	1.3466	0.9615	1.4963
	CPO	1.4198		
60	CHO	1.4035		
	THF	—	0.9524	1.4916
	CPO	1.4365		

the hydrodynamic volume obtained are in the order of the solvent power determined before. The decrease in hydrodynamic volume with increase in temperature may be because of the decrease in interaction between polymer-solvent molecules leading to contraction of the coil. The hydrodynamic volume is higher in high molecular weight sample which is obvious from the fact that with increase in molecular weight the volume occupied by the molecule itself also increase.

Unperturbed chain dimension

The unperturbed chain dimensions of the PVC with respect to different temperature were determined using Deb and Chatterjee equation (1). In the absence of a theta solvent this equation seems to be quite useful for the determination of the unperturbed chain dimension. The values of the unperturbed chain dimension obtained in this way are shown in Table-5. These values are slightly higher than the reported values [15]. This difference may be due to the fact that they used extrapolation method the Stockmayer-Fixman equation [16] which gives K_θ values and from this unperturbed chain dimension were calculated in one polymer-solvent system, while in our case the $1/[\eta]$ values of three different solvents are plotted against K_H to get $1/[\eta]_K$ which is then introduced in equation 1 and then we get the unperturbed chain dimension values. These values of unperturbed chain dimension are characteristic of the given species and a measure of chain flexibility. They are independent of the solvent which is the reason why

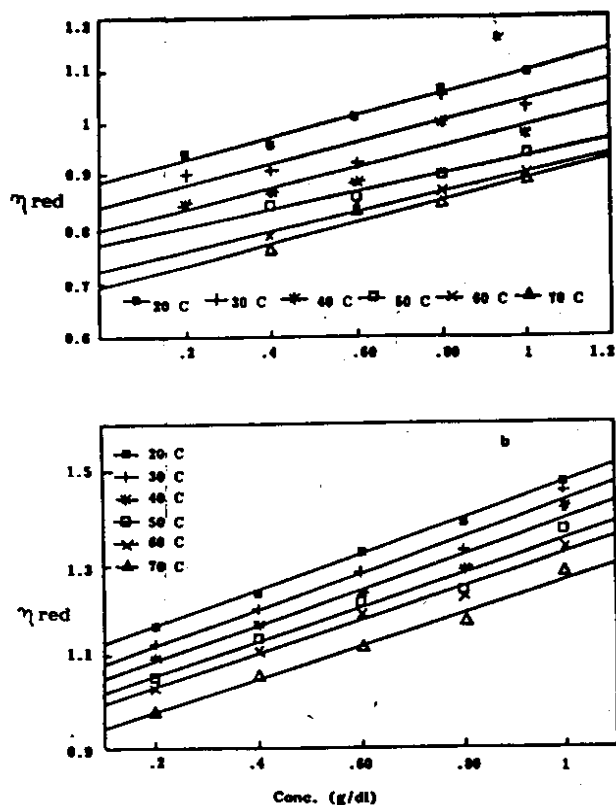


Fig. 1: Plot of reduced viscosity vs concentration of PVC-Cyclohexanone system at different temperatures (a. Mw. 100,000; b. Mw. 200,000).

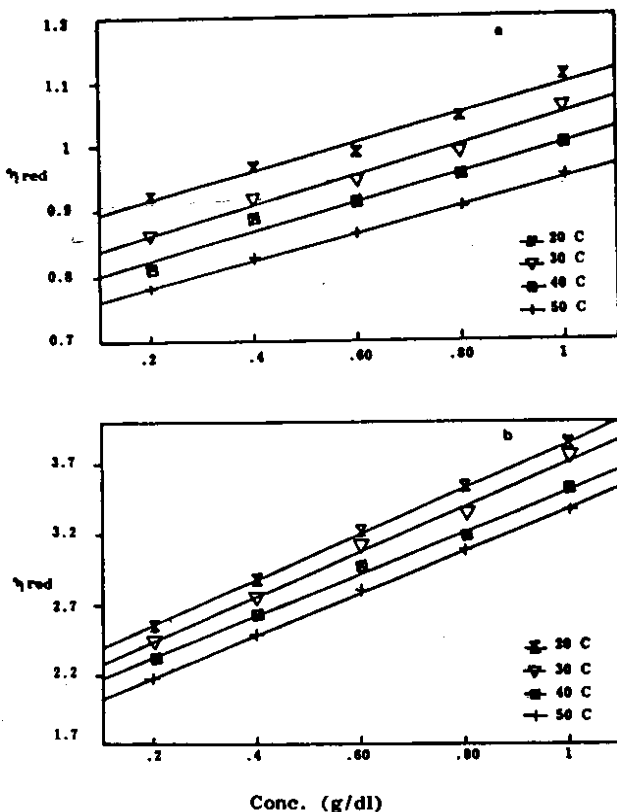


Fig. 2: Plot of reduced viscosity vs concentration of PVC-Tetrahydrofuran system at different temperatures. (a. Mw. 100,000; b. Mw. 200,000).

$1/[\eta]$ of three different solvents-PVC system are plotted against K_H in Deb and Chatterjee equation.

Experimental

Two different molecular weight samples of PVC supplied by BDH Pool England were used without fractionation and purification. The solvent used were Cyclohexanone (CHO), Cyclopentanone (CPO), Dioxane (DIOX) and Tetrahydrofuran (THF), from Merck. All the solvents were once fractionally distilled. All the solutions were prepared at 25°C and, with the exception of low boiling tetrahydrofuran solutions, were heated at 70-80°C for about one hour. This preliminary heating was necessary to obtain complete molecular dispersion [9].

Viscosities of the solvent and the solutions in the concentration range 0.2-1.0 g/dl were

measured at 20-70°C, using an Ubbelohde viscometer of type OB.

Intrinsic viscosity $[\eta]$ and Huggin's constant K_H were determined using Huggin's equation [10].

$$\eta_{red} = [\eta] + K_H [\eta]^2 C \dots\dots\dots(2)$$

where η_{red} = reduced viscosity; K_H = Huggin's constant.

$[\eta]$ = Intrinsic viscosity and

C = Concentration in g/dl

Various plot of η_{red} vs concentration are given in Figures 1-4. The values of $[\eta]$ and K_H obtained from these plots are summarized in Table-1.

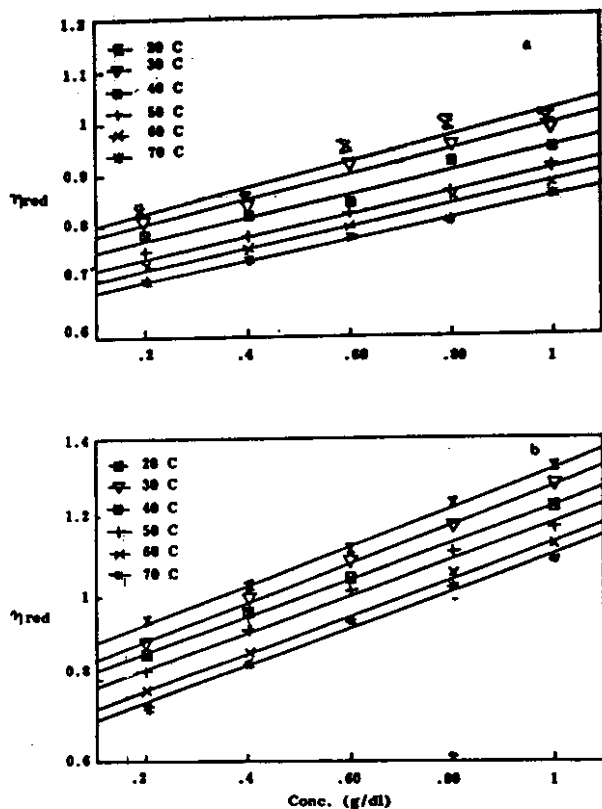


Fig. 3: Plot of reduced viscosity vs concentration of PVC-Cyclopentanone system at different temperatures. (a.Mw. 100,000; B. Mw. 200,000).

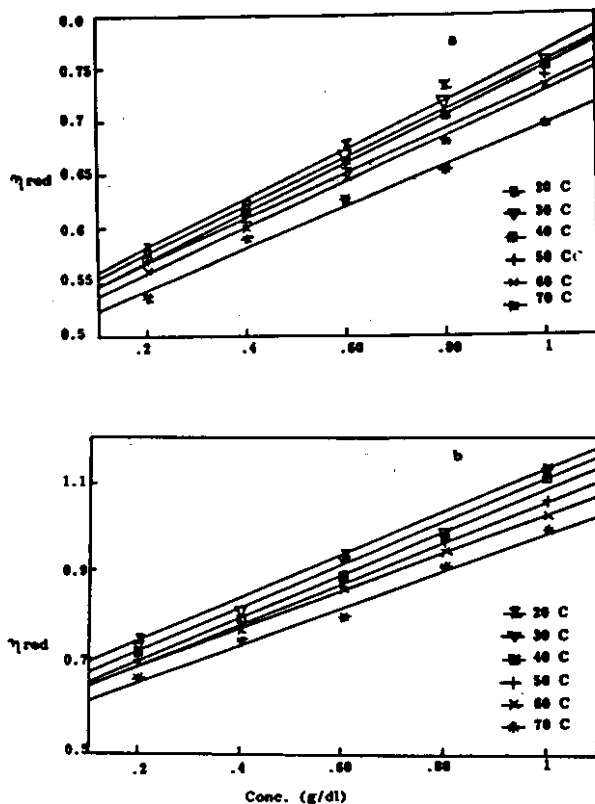


Fig. 4: Plot of reduced viscosity vs concentration of PVC-Dioxane system at different temperatures. (a.Mw. 100,000; b. Mw. 200,000).

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