ULTRASONIC STUDY OF MOLECULAR ASSOCIATION OF AQUEOUS SOLUTIONS OF POLY(VINYL ALCOHOL). A METHOD TO DETERMINE MOLECULAR WEIGHT

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Abstract—Ultrasonic velocity and iso-entropic compressibility measurements are reported for aqueous solutions of poly(vinyl alcohol) (PVA) of various molecular weights and various concentrations using a pulsed ultrasonic apparatus operating at 2 MHz and 303 K. The data obtained as a function of concentration indicate the magnitude of the contributions due to relaxation of the backbone and of the side-chain acetyl group. The results show a linear increase of velocity, density and viscosity with increasing molecular weight and concentration of PVA. In contrast, the iso-entropic compressibility decreases with increasing molecular weight and concentration of PVA. This suggests interaction between PVA and water molecules. A mathematical equation correlating iso-entropic compressibility and molecular weight of the polymer is suggested. It was applied to calculate the molecular weight of four unknown samples of PVA from their measured iso-entropic compressibility. The results agree well with those obtained from osmometry.

1. INTRODUCTION

Poly(vinyl alcohol) (PVA) is a synthetic water soluble polymer [1], the hydroxyl groups conferring on the polymer both donating and accepting power in formation of hydrogen bonds. Investigations of the solution properties have indicated that there is the possibility of gelation and recrystallization phenomena in this system [2]. Studies of the i.r. spectrum of PVA in the solid state [3] have established the existence of both inter- and intra-molecular hydrogen bonds. Investigations of the viscosity and related properties have been used to infer the existence of intra-molecular hydrogen bonding, so strong that urea cannot break them [4]. The specific interaction between solvent and polymer may influence the dynamics of the polymer chain. Solvent effects clearly have a large influence on the properties of PVA and so might influence the ultrasonic relaxation behaviour.

2. EXPERIMENTAL

2.1. Materials

Six samples of PVA supplied by Aldrich, having different molecular weights and residual acetate contents, were used. Their characteristics are summarized in Table 1. The materials were used without further purification. Solutions were prepared by adding a known weight of the polymer to a fixed volume of water and then boiling under reflux with magnetic stirring for 30 min. The solution was then cooled to room temperature, giving a clear solution.

2.2. Ultrasonic measurements

Attenuation data were obtained using the pulsed ultrasonic technique (PHYWE, West Germany). The method of measurement and temperature control have been described [5]. The accuracy of the velocity measurements was ± 0.15%, and the temperature was measured with a precision of ± 0.1 K using a digital thermometer.

2.3. Density measurements

The densities of the solutions were determined using a digital densitometer, Anton Paar DMA 60, with a precision of ± 0.01%. The technique has been described [6].

2.4. Viscosity measurements

The viscosities of the solutions were determined using an OSTWALD viscometer thermostated to ± 0.1 K. The procedure has been described [7]; the accuracy of the measurements was ± 0.015%.

2.5. Theoretical calculations

The Laplace relationship was used to calculate the iso-entropic compressibility, $\beta_i = 1/\rho \cdot v^2$, where ρ is the density and v is the longitudinal sound velocity [8].

2.6. Vapour pressure osmometry (VPO)

The number-average molecular weights ($\bar{M}_n$) of PVA samples were measured using a Knauer vapour pressure osmometer. The technique has been described [9]. The accuracy in $\bar{M}_n$, values thus determined was ± 5%.

3. RESULTS

The results of the measurements for the acoustic attenuation for different molecular weights and concentrations of aqueous solutions of PVA are shown in Figs 1–4.

Table 1. The characteristics of poly(vinyl alcohol) samples

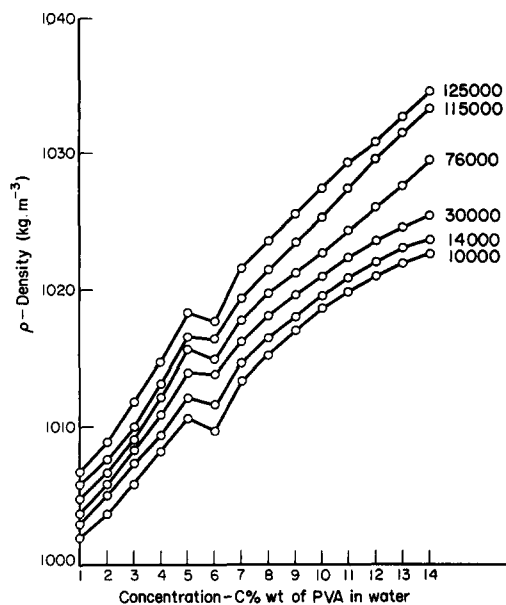| Sample code No.	$\bar{M}_n$	Degree of hydrolysis (%)
S_1	10,000	88
S_2	14,000	88
S_3	30,000	88
S_4	76,000	88
S_5	115,000	100
S_6	125,000	88

Fig. 1. Density vs concentration of PVA in water for various molecular weights.

Increases in molecular weight and concentration of PVA in solution brought about increases in density, velocity and viscosity (Figs 1–3). Increases of concentration and $\bar{M}_n$ of PVA in solution were accompanied by a decrease in the iso-entropic compressibility (Fig. 4).

4. DISCUSSION

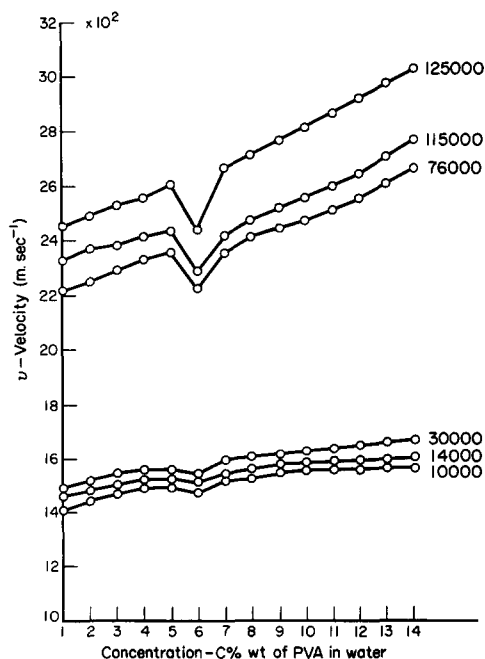The decrease in iso-entropic compressibility with increasing concentration for a constant frequency

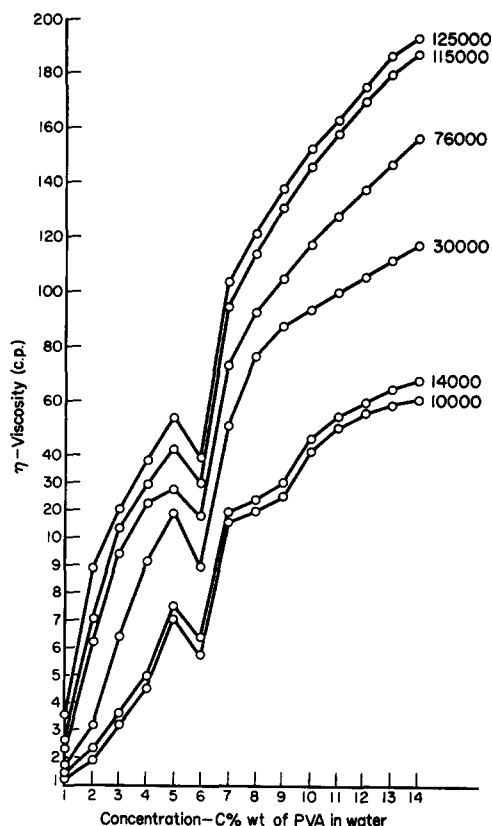Fig. 3. Viscosity vs concentration of PVA in water for various molecular weights.

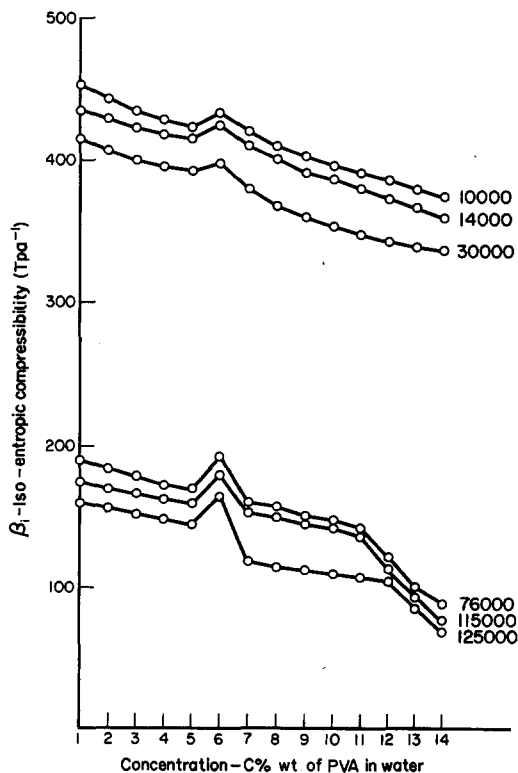Fig. 2. Velocity vs concentration of PVA in water for various molecular weights.

Fig. 4. Iso-entropic compressibility vs concentration of PVA in water for various molecular weights.
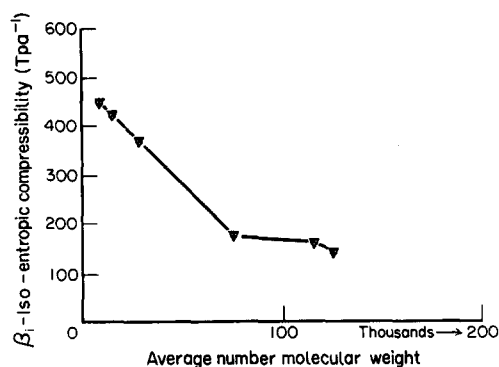
Fig. 5. Iso-entropic compressibility vs molecular weight of PVA. ×, 2%; ○, 3%; ▽, 4%.

of 2, 3 and 4% were correlated (Fig. 5) and the following relationship was suggested:

$$\beta_i = a_0 + a_1 \bar{M}_n + a_2 \bar{M}_n^2,$$

where a_0, a_1 and a_2 are constants determined, using IBM-4341 computer, as $a_0 = 0.5224 \times 10^3 \, \text{Tpa}^{-1}$; $a_1 = -0.5892 \times 10^{-2} \, \text{Tpa}^{-1}$; $a_2 = 0.2386 \times 10^{-7} \, \text{Tpa}^{-1}$; and the root-mean-square of the errors is $0.0215 \times 10^2 \, \text{Tpa}^{-1}$. To examine the validity of this correlation, four other unknown samples of PVA were used, with molecular weights previously determined by VPO. The iso-entropic compressibilities of these samples at 2, 3 and 4% concentrations were determined using the ultrasonic technique, and values of $\bar{M}_n$ were calculated by the suggested equation. The results agree well with those determined by VPO, as illustrated in Table 2.

was probably due to a modification in the nature of the intra-molecular interaction [10]. A further increase in concentration led to deviation from a simple linear dependence, probably indicating entanglement interactions.

The interaction causing association between different molecular weights of PVA and water may be responsible for the increase in ultrasonic velocity and the decrease in iso-entropic compressibility, possibly because the polymer molecules come close to the solvent molecules leaving space around them [10].

Figures 1–4 show an inflection point at 6%. This corresponds to the gel point of the solution at 6%, with some individual polymer molecules existing in the solution. As the concentration is increased, the extent of the interaction increases; above and below this critical concentration, the hydrogen bonds between polymer molecules can lead to the formation of a network and the possibility of gelation [11].

5. CONCLUSION

The ultrasonic studies on PVA solutions indicate that, as with other polymers in solution, a variety of processes can be identified. In particular, the low frequency spectrum indicates the motion of the side-chains dominated by backbone and normal mode motion [11] whereas the higher frequency spectrum refers to the motion of the side-chains.

In addition, this study has allowed identification of polymer–solvent interaction. Results show that, at 6% concentration of PVA in water, there is a molecular aggregation as shown in all curves of Figs 1–4.

The iso-entropic compressibility and number-average molecular weight of PVA at concentrations

Table 2. A comparison between $\bar{M}_n$ values measured by VPO and values calculated using the proposed equation

Sample code	$\bar{M}_n$ by VPO		β_i (Tpa^{-1})	$\bar{M}_n$ by calculation	% Error
1	2000	2%	510.7286	1994	0.3
		3%	510.7228	1995	0.25
		4%	510.7171	1996	0.2
2	3000	3%	505.0241	2982	0.6
		3%	505.0241	2982	0.6
		4%	504.9896	2988	0.4
3	16,000	2%	435.0344	15,840	1.0
		3%	434.8701	15,872	0.8
		4%	434.7058	15,904	0.6
4	95,000	2%	179.5281	93,860	1.2
		3%	179.2604	94,050	1.0
		4%	178.9945	94,240	0.8

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