Ultrasonic studies of aqueous solutions of polyvinylalcohol

Abdul Abu-Bakr and Richard A. Pethrick*
Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, UK

and Jacques Emery
Department of Physics, Université du Main, Route Laval, Le Mans, France

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Ultrasonic absorption and velocity measurements are reported on aqueous solutions of polyvinylalcohol of different molecular weights, degrees of hydrolysis and concentration. The absorption measurements cover a frequency range from 2–1000 MHz and the velocity data a frequency range from 2–200 MHz, the data were obtained over a temperature range from 273 to 333 K. Comparison of the data obtained as a function of the degree of hydrolysis indicate the magnitude of the contributions due to relaxation of the backbone and of the side chain acetyl groups. In the case of the 100% hydrolysed material, the relaxation spectrum is simplified and corresponds to that of motion of the pendant hydroxyl groups. Deviations of the variation of the attenuation with concentration from the 'ideal' dilute solution behaviour are ascribed to the effects of polymer–polymer interactions. The magnitude of the volume change associated with polymer–solvent interactions is estimated and discussed.

Keywords Ultrasonic; polyvinyalcohol; solvation; normal mode, conformational isomerism

INTRODUCTION

Polyvinylalcohol is interesting from several aspects. It is one of the simplest of the synthetic water soluble polymers[1], the hydroxyl groups conferring on the polymer both donating and accepting power to and from hydrogen bonds. Commercially polyvinylalcohol, PVA, is synthesised by the hydrolysis of polyvinyl acetate; since the hydrolysis is difficultto take to completion a number of partially hydrolysed polymers containing residual acetate groups carry the name of PVA[1-3]. Investigations of the solution properties have indicated that there is the possibility in this polymer system of gelation and recrystallization phenomena. The variation of the water solubility of PVA highlights the effects of residual acetate groups on the properties of this polymer. A 50% hydrolysed polyvinylacetate is insoluble in cold water and in aqueous ethanol and acetone but is soluble in hot water, showing an upper consulate temperature. Between 75 and 80% hydrolysis the material loses its solubility in mixed solvents. Between 80 and 90% hydrolysis it is soluble in hot and cold water. Finally, for 98–100% hydrolysed material contact with cold water only produced swelling but solution can be achieved with hot water. However, if the solutions are sufficiently concentrated a gel is formed on cooling. It is therefore very clear that interactions between polymer and solvent are very marked in this system.

Recent measurements of the acoustic relaxation of polystyrene in toluene[4] and various hydrocarbon solvents have indicated that the position and amplitude of the relaxation associated with rotational isomerism is sensitive to the type of solvent used. A variety of explanations have been proposed to explain this effect. Since the amplitude of the ultrasonic relaxation is proportional to the energy difference between states it is possible that the difference may be in part attributed to the effects of changes in the dielectric constant on the energy difference[5]. Attempts to explain the observed effects on this basis have failed[4]. It is possible to invoke the viscosity of the solvent as impeding the rotational isomerism and as a result it will lead to an increase in the activation energy associated with this process. Spin probe measurements have tended to support this hypothesis[6]. However, in general, this may not explain the whole of the observed effect. An alternative proposition is that specific interactions 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 as such might be expected to influence the observed ultrasonic relaxation behaviour.

Investigations of the infra-red spectrum of PVA in the solid state[7] have established the existence of both inter- and intramolecular hydrogen bonds. Investigations of the viscosity and related properties have been used to infer the existence of intramolecular hydrogen bonding[8] so strong that urea cannot break them. Treatment with 6% NaOH solution can disrupt these linkages. However, it may also initiate some degradation of the polymer.

Ultrasonic relaxation of the parent polymer, polyvinylacetate, has been reported both in toluene and acetone solution[9,10]. In toluene solution, two relaxations are observed, the first occurring at a frequency of approximately 6 MHz at 293K and a second relaxation at 60 MHz. The amplitude of the lower frequency process is comparable to that observed in polystyrene[4]. Investigations of the variation of the position of this relaxation with length of the alkyl group in the series of

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Table 1 Molecular weight characteristics of polyvinylalcohol samples

Code	Degree of hydrolysis %	Molecular weight M_w
S1	100	115000
S2	88	125000
S3	88	96000
S4	88	10000
S5	75	3000

Table 2 Relaxation characteristics of polyvinylalcohol solution

		Relaxation characteristics			
Code	Concentration (% w/w)	*A* $(\alpha/f^2) \times 10^{15}$ ms²	*B*	f_c (MHz)	Temperature (K)
S1	3	6.1	24.5	113	293
S2	3	35	25	32.5	293
S3	3	30.6	24	32.5	293
S4	3	28.4	24	30	293
S5	3	184	80	1.42	293
	3	370	72	1.02	303
	3	150	56	1.8	313
	3	100	44	2.50	323
	3	74	37	2.74	333
	5	350	75	1.7	293
	5	255	80	1.99	303
	5	150	70	2.40	313
	10	1600	140	0.77	293
	10	430	210	1.79	303
	10	306	20	5.30	313
	10	220	20	12.7	323
	10	185	18	17.3	333
S5	15	1300	120	1.67	293
	15	1000	20	1.85	303
	15	810	18	2.12	313

polymers: polyvinylacetate, polyvinylpropionate and polyvinylbutyrate, indicates that the relaxtion frequency varies approximately as the inverse square root of the moment of inertia of the side chain indicating that the relaxation is associated with segmental motion of the backbone. Funfshilling, Lemarechal and Cerf[10] have suggested that these relaxations are due to two local internal motions of the chain backbone, one involving a large number of units the other a smaller number of units. Nomura *et al.*[11] have preferred an alternative explanation in which the higher frequency process is ascribed to motion of the alkyl side chain. Support for this hypothesis can be found if one compares the amplitude of the observed process with that reported from ultrasonic studies of normal alkanes[12]. The amplitude and position are consistent with the higher frequency process being ascribed to rotation of the side group.

EXPERIMENTAL

Materials

The polyvinylalcohols used in this study were obtained from Aldrich Chemical Company; their characteristics are summarised in *Table 1*. These 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 thirty minutes. The solution was then cooled to room temperature whereupon a clear solution was obtained.

Ultrasonic experiments

Attenuation data was obtained using a combination of a low frequency acoustic resonator, 2–10 MHz[13], pulsed acoustic apparatus to cover the frequency ranges 15–65 MHz[14] and 150–1000 MHz[15]. The velocity measurements were performed using an acoustic interferometer at 2–10 MHz[16] and a Bragg diffraction apparatus from 40–200 MHz[17]. Temperature was measured with a precision of ±0.1K using a digital thermometer. The data obtained were analysed using a PDP computer and fitted to a series of single relaxations[18]. The relaxation characteristics are summarised in *Table 2*.

Density data

The densities of the solutions were determined using a digital densitometer, Anton Paar DMA 60 and have a precision of ±0.01%. The technique has been described elsewhere[18].

Viscosity measurements

The viscosities of the solutions were determined using a suspended level viscometer thermostated with a precision of ±0.1K. The method of measurement has been described elsewhere[18].

RESULTS AND DISCUSSION

Effect of degree of hydrolysis

Polyvinylalcohol is obtained commercially by the hydrolysis of polyvinyl acetate and as a consequence partially hydrolysed polymer will contain a significant quantity of residual acetyl groups. The acoustic attenuation data for 100%—S1, 88%—S2 and 75%—S5 are presented in *Figures 1–3*. Comparison of tne amplitudes of the relaxations at 293K indicates that as the degree of hydrolysis is reduced so the amplitude of the relaxation is increased. In S1 a small amplitude relaxation is observed

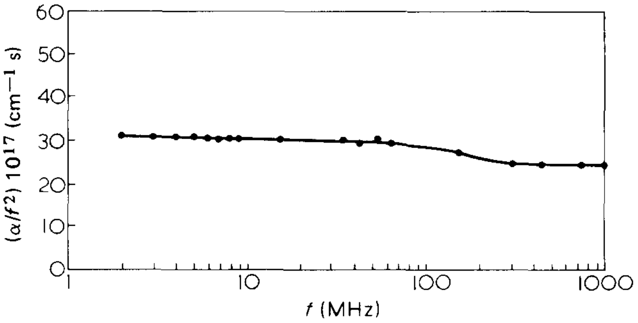

Figure 1 Acoustic attenuation for a 3% solution of 100% hydrolysed PVA (M_w 115000) at 293K

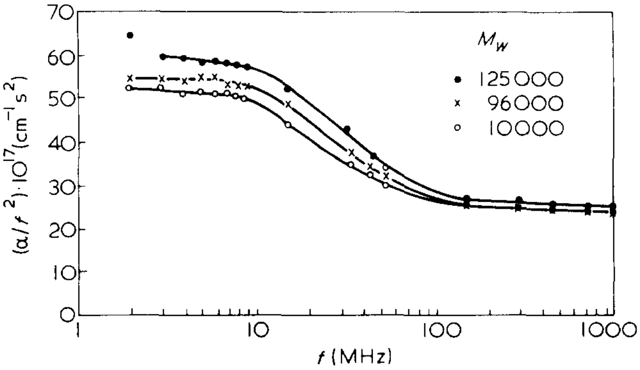

Figure 2 Acoustic attenuation for a 3% solution of 88% hydrolysed PVA at 293K, M_w 125000 (●); 96000 (X); and 10000 (O)

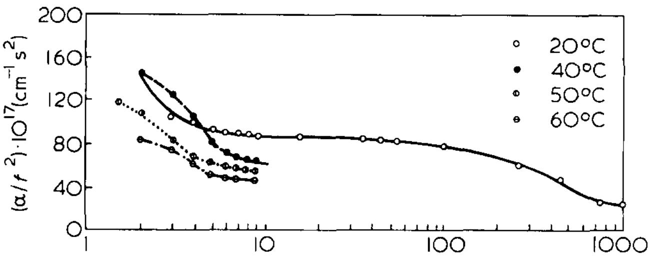

Figure 3 Acoustic attenuation for a 3% solution of 75% hydrolysed PVA, M_w 3000 at 293K (○); 313K (●); 323K (○) and 333K (○)

with characteristic frequency of approximately 120 MHz; in S2 the amplitude of the relaxation is increased and the frequency decreased to approximately 30 MHz. It is also noticeable that a decrease in the molecular weight of the polymer leads to a decrease in the amplitude of the relaxation without a change in the characteristic frequency. This type of behaviour is typical of segmental relaxation of the backbone of a vinyl polymer. Similar behaviour has been reported for polystyrene in toluene and is attributed to differences in mobility of the ends of the polymer relative to the centre of the chain. This observation would lead to the proposition that this relaxation is probably dominated by rotational isomerism of the backbone. In S5, the amplitude of the relaxation is increased further and the frequency is decreased as a consequence of the increase in the acetyl concentration. This is probably a result of interactions between the pendant acetyl and certain of the hydroxyl groups. The high frequency process above 100 MHz occurs in the same region as that observed for the side group motion in the pure polyvinylacetate polymer and is also of comparable amplitude.

Examination of the variation of the viscosity with reciprocal temperature (*Figure 4*) indicates that the activation energy for viscous flow changes at approximately 323K. Since the presence of the residual acetate groups weakens hydrogen bonding between intra- and intermolecular hydroxyl groups the solubility of partially hydrolysed PVA in water is higher than that of fully hydrolysed PVA. Residual acetate groups as high as 20 mol per cent (80 per cent hydrolysed) at low temperature increase the solubility. However, at high temperatures owing to a decrease in the temperature of phase separation, solubility is decreased. Studies of the effects of concentration on the viscosity shows an inflection point at 3%. It has further been observed[1] that the apparent activation energy shows a secondary inflection at 10–12 per cent, this corresponding to the gel point of the solution. Below 3% individual polymer molecules exist in the solution. However, above this concentration significant interaction occurs between individual polymer molecules. As the concentration is increased so the extent of the interaction increases. Above the second critical concentration of 10–12 per cent, the hydrogen bonds between polymer molecules can lead to the formation of a network and the possibility of gelation exists. Increasing the temperature has the effect of changing the distribution of intramolecular interactions and hence the conformation and size of the polymer in solution. It is observed from *Figure 4* that the temperature of the kink changes with concentration. Using the data from the shear viscosity it is possible to calculate the contribution due to normal mode relaxation to the ultrasonic attenuation[4]. In the present case, this makes a contribution of less than 10 to the observed attenuation, supporting the hypothesis that the major contribution to the low frequency attenuation arises from conformational changes of the polymer backbone. The limiting high frequency asymptotic value of the attenuation versus frequency is close to that of pure water indicating that the polymer does not significantly influence the structural relaxational contribution to the attenuation of the solvent.

A close examination of the attenuation curves for S5 indicates that as the temperature is increased the amplitude of the absorption is initially increased and then decreases. This behaviour is similar to that observed in polystyrene[4] and polyisobutylene[19] and is indicative of a sudden loss of structure in the backbone with increasing temperature. In this case the loss of structure may be attributed to a destruction of hydrogen bonding interactions between hydroxyl and acetate groupings.

Effects of concentration on the relaxation behaviour

The variation of the ultrasonic relaxation as a function of concentration at 293K is shown in *Figure 5*. A marked increase in the attenuation is observed at low frequency; the calculated contribution at 3, 5, 10, 15% due to shear-normal mode relaxation being respectively 10, 20, 135 and 420×10^{-17} m^2 s. The increase observed is therefore paralleled by the change in the viscous contribution. Dividing the shear contribution by the concentration indicates that the increase in attenuation is directly proportionate to the amount of polymer present. Subtracting the contribution due to normal mode motion and plotting the residual against concentration indicates that the attenuation initially decreases and then increases. The initial decrease is probably due to a modification in

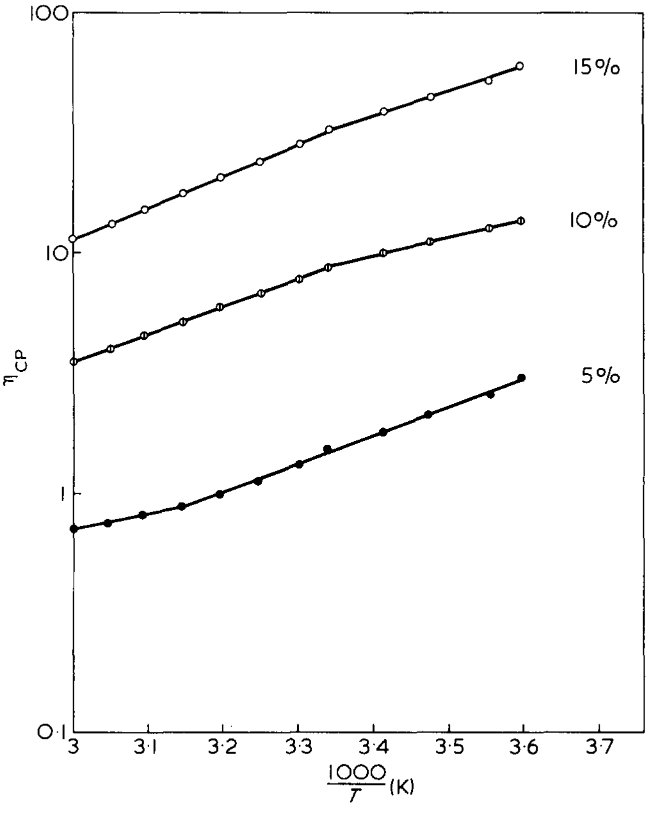

Figure 4 Variation of the viscosity as a function of temperature and concentration for 75% hydrolysed 3000 M_w PVA

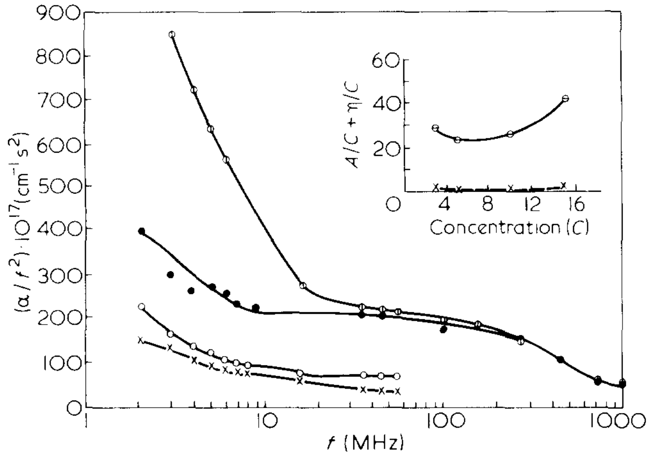

Figure 5 Acoustic attenuation for 75% hydrolysed PVA M_w 3000 at 293K for 3 (X); 5 (○); 10 (●) and 15 (○)

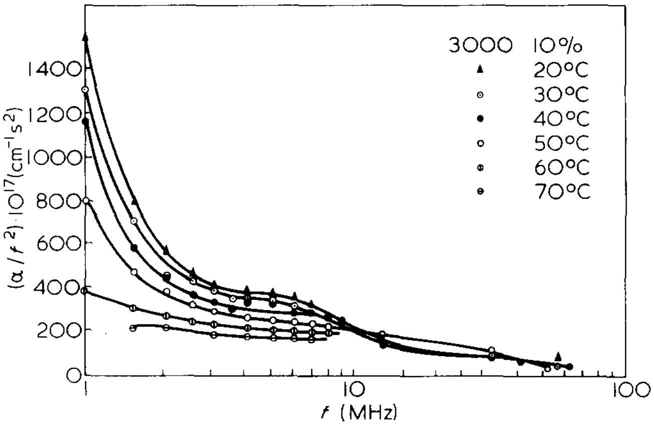

Figure 6 Acoustic attenuation as a function of temperature for a 10% solution of 75% hydrolysed PVA, 3000 M_w. (▲) 293K; (○) 303K; (●) 313K; (○) 323K; (○) 333K and (○) 343K

the nature of the intramolecular interactions with change in concentration. Further increase in concentration leads to a deviation from a simple linear dependence and is indicative of polymer entanglement interactions, prior to gel formation. Similar deviations have been observed for variation of the acoustic attenuation of polydimethyl siloxant and polystyrene[20,21] with concentration. In these latter systems, the deviations have been attributed to entropic fluctuations associated with the incipient network formation.

Effect of temperature on the relaxation spectrum

The variation of the acoustic attenuation with frequency and temperature for 10 and 15% solutions of PVA are shown in *Figures 6* and *7*. Analysis of the low frequency dispersion indicates that the relaxation frequency does not vary linearly with reciprocal temperature. However, subtraction of the normal mode contribution calculated from the measured viscosity produces a relaxation whose characteristic frequency does vary linearly with reciprocal temperature, *Figure 8*. The way in which the normal mode and segmental processes interact can be appreciated by plotting the time constant of the first normal mode and that of the characteristic frequency for the low frequency relaxation, *Figure 9*. It can readily be appreciated that at approximately 303K both processes have comparable time constants and hence a probably strong mixing of the processes. Shifting the temperature leads to a separation of these processes. This point is also reflected in the concentration dependence of the activation energies for ultrasonic relaxation and viscous flow, *Table 3*.

The activation energy for viscous flow increases with concentration as expected and is indicative of increasing interaction between polymers. At about 3% the activation energy for viscous flow and segmental motion are comparable as would be expected from the comparability of relaxation times. Increase in concentration shifts the normal mode process to lower frequencies and the decoupling of the two processes leads to the observed reduction in the activation energy to one which is similar to that for alkane backbone motion[12].

The above observations are consistent with there being

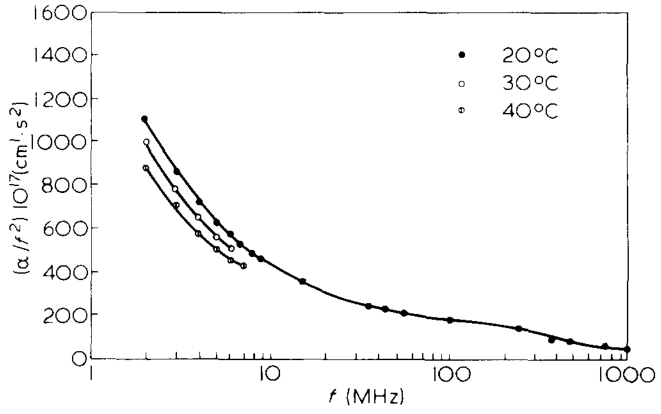

Figure 7 Acoustic attenuation as a function of temperature for a 15% solution of 75% hydrolysed PVA, 3000 M_w. (●) 293K; (○) 303K; (○) 313K

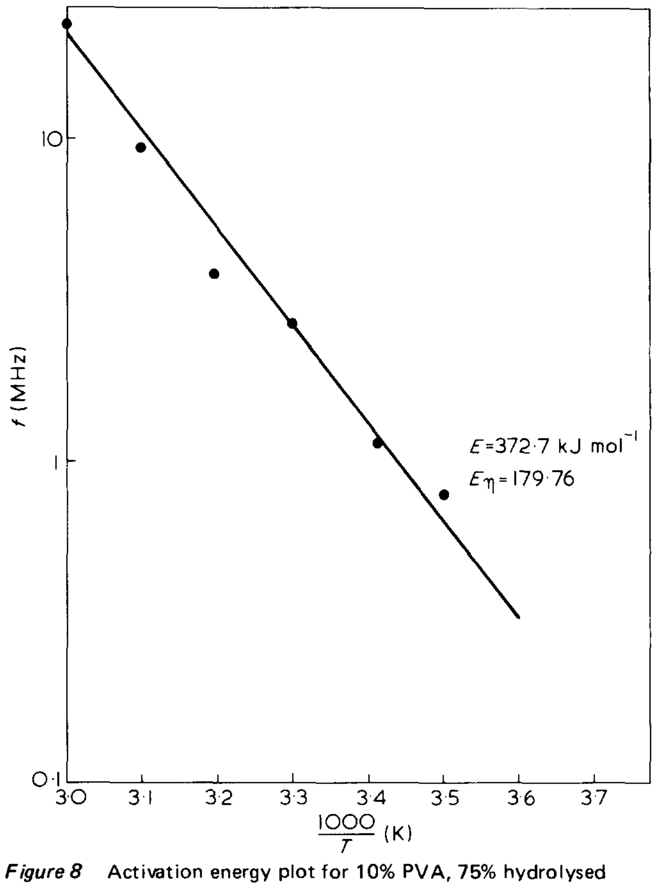

Figure 8 Activation energy plot for 10% PVA, 75% hydrolysed 3000 M_w

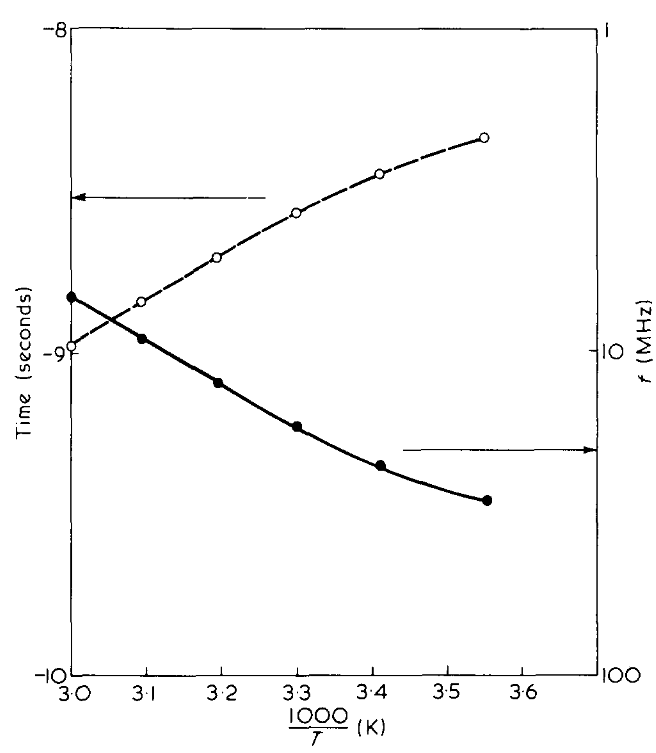

Figure 9 Plot of the normal mode relaxation time and the characteristic time for the low frequency relaxation as a function of reciprocal temperature

Table 3 Activation energies for PVA 3000 M_w 75% hydrolysed

Concentration (% w/w)	E (kJ mol^{-1})	E_{viscous} (kJ mol^{-1})
3	34.7	26.4
5	29.1	65.6
10	37.2	179.7
15	15.3	798.1

two relaxations; a low frequency process associated with rotational motion of the segments of the polymer backbone—this process in certain situations appears to be closely coupled to normal mode relaxation, and a higher frequency process associated with motion of the side chains.

Velocity data on polyvinyl alcohol solutions

Examination of the frequency dependence of the velocity in a 10% solution of S5 at 273 and 283K (*Figure 10*) indicates the existence of a marked increase in the high frequency velocity which apparently does not have a counterpart in the attenuation (*Figure 7*). It is assumed that the characteristic relaxation frequency is approximately 200 MHz then the velocity dispersion corresponds to 8 m s^{-1}. The major effect of changing temperature was observed to be a shift in the baseline value of the velocity associated with a change in the compressibility of the solvent-water. The Laplace relationship can be used to calculate the isoentropic compressibility, $K = 1/\rho c^2$ where ρ is the density and c is the longitudinal sound velocity. The observed incremental corresponds to approximately 0.5% change in the isoentropic compressibility. For a 10% solution this corresponds to a loss in compressibility of one molecule of water per chain element. Clearly this implies that the solution probably involves more than one monolayer

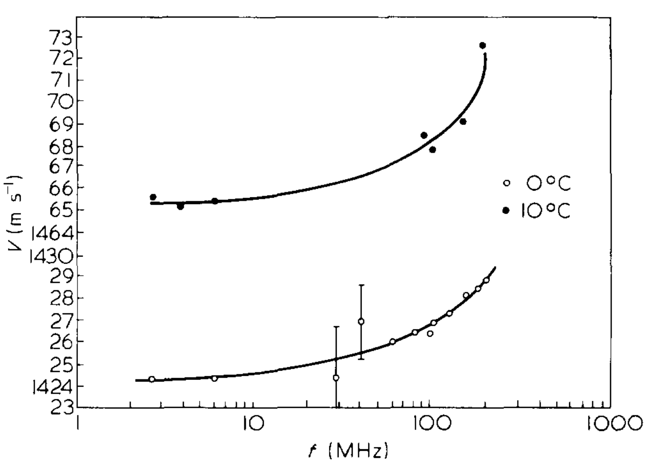

Figure 10 Velocity dependence as a function of frequency at 273 and 283K for a 10% solution of PVA 75% hydrolysed 3000 M_w

since the polymer investigated is only 75% hydrolysed. The position of the relaxation does not vary rapidly with temperature indicating a low activation energy which is consistent with a hydrogen bond exchange process.

CONCLUSIONS

The ultrasonic studies on polyvinylalcohol solutions indicate that as with other polymers in solution a variety of processes can be identified. In particular, the low frequency spectrum is dominated by backbone and normal mode motion, whereas the higher frequency spectrum reflects the motion of the side chains. In addition, this study has allowed identification of polymer–solvent interaction and also allowed the contribution to the total compressibility to be determined.

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