

The effects of hydrogen bonding upon the viscosity of aqueous poly(vinyl alcohol) solutions

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Received 2 February 1998; received in revised form 27 January 1999; accepted 30 July 1999

Abstract

This paper describes the rheological properties of a number of aqueous solutions of a poly(vinyl alcohol) (PVA) as a function of the degree of polymer hydrolysis, ambient temperature, pressure and variations induced upon the addition of electrolytes to these solutions. Experimental results reported show that the rheological behaviour of these aqueous PVA solutions mainly depends upon the relative strength of the hydrogen bonding existing between the polymer chains and water molecules, compared with that of the inter and intra chain hydrogen bonding. Changes in temperature, pressure, degree of hydrolysis of the PVA, and the addition of electrolytes produce a corresponding effect in varying these two types of hydrogen bonding and thus the resulting rheological properties of the PVA solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PVA; Rheology; Aqueous solution

1. Introduction

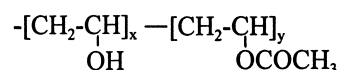
Poly(vinyl alcohol) (PVA) was one of the first synthetic polymers to be produced on a large scale commercially and has been developed and utilised in various industrial applications. Amongst these are the use of PVA as an emulsifier and as a stabiliser for colloid suspensions, as a sizing agent and coating in the textile and paper industries, and as an adhesive [1–4]. The control and rationalisation of the origins of the viscosity of aqueous PVA solutions is naturally important in these industrial applications. It has been reported previously that the viscosity of aqueous PVA solutions is determined mainly by the polymer molecular weight and polymer concentration [1,2,5–7].

There is some agreement that the viscosity of aqueous solutions of a similar polymer, poly(ethylene oxide) (PEO), is closely related to the extent of hydrogen bonding between the PEO chains and water molecules [8,9]. The extent of hydrogen bonding decreases with increase in temperature and pressure, and with addition of electrolytes into the solution, which leads to a reduction of the “solvent quality” of water. Thus, the viscosity of PEO solutions

decreases with increase in temperature and pressure, and presence of electrolytes. For PVA, however, it has been shown that, in addition, there is also a strong and influential inter and intra chain hydrogen bonding formed between the polar hydroxyl groups in the PVA molecules [10]. In aqueous PVA solutions, a part of this hydrogen bonding remains, in addition to the hydrogen bonding between the PVA chains and the water molecules formed newly upon dissolution [1,2,11,12]. The extent of both inter and intra chain hydrogen bonding, and solute–solvent hydrogen bonding is mainly determined by the degree of hydrolysis in the PVA chains, which is simply defined as the following:

$$\text{Degree of hydrolysis} = \frac{x}{x+y} \times 100\% \quad (1)$$

where x and y are the molar fractions of the hydroxyl and the acetate groups, respectively, specified in the following stoichiometric formula:



Thus, it is expected that these two kinds of hydrogen bonding will play an important role in determining not only the solubility of the PVA solutions but also the viscosity of the corresponding solutions. In this work, a similar method to that reported by the present authors in previous studies of aqueous PEO solutions has been adopted to study

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Table 1
Specification of PVA

Supplier	Molecular weight ($\times 1000$)	Degree of hydrolysis (%)	Degree ^a of polymerisation	Code
Aldrich, UK	100.000	88	2039	PVA-100-88
BDH, UK	72.000	98	1605	PVA-72-98
Harco, UK, Mowiol 3-83	14.000	83	274	PVA-14-83
Harco, UK, Alcotex 78%	37.500	78	704	PVA-37.5-78
Harco, UK, Alcotex 72.5%	37.500	72.5	675	PVA-37.5-72.5

^a Degree of polymerisation is calculated from the value of molecular weight and degree of hydrolysis provided by suppliers.

the potential influence of hydrogen bonding upon the rheological properties of aqueous PVA solutions. The advantage of using the PVA system is that the extents of both inter and intra chain hydrogen bonding and solute–solvent hydrogen bonding can be adjusted by variation of the degree of hydrolysis of the PVA. This variable complements the variables adopted in the work on the rheology of aqueous PEO solutions [8,9]. This stoichiometric variable provides an important additional variable for the current study, and hence a further understanding of the role of hydrogen bonding in controlling the properties of aqueous solutions of polymers, such as solubility, phase behaviour and viscosity.

2. Experiment

2.1. Materials

The specifications of the PVA materials, as provided by the different suppliers, used in this work are summarised in Table 1. An abbreviation, PVA-X-Y, is adopted to characterise polymer molecular weight and degree of hydrolysis; X is the molecular weight (in 1000s) and Y is the degree of hydrolysis. For example, PVA-100-88 represents a PVA with a molecular weight of 100,000 and a degree of hydrolysis of 88%. Analytical grade sodium chloride, as supplied by Aldrich Co. (UK), and de-ionised water were used in the preparation of the PVA solutions.

2.2. Preparation of polymer solutions

Aqueous polymer solutions were prepared by dispersing the “as received” polymer powder into de-ionised water under mild mixing conditions. The polymers in aqueous electrolyte solutions were prepared by dispersing the polymer powder into pre-prepared aqueous electrolyte solutions, also under mild mixing condition. For PVA solutions with high degrees of hydrolysis, above 88%, heating to at least 80°C was necessary to fully dissolve the sample. Corrections for solvent evaporation were made for all the preparations. The concentrations of the polymer solutions were

calculated and reported as a weight percentage of the formulation.

2.3. Experimental methods

A Bohlin VOR viscometer (Bohlin Reologi, Sweden), and a high temperature and high-pressure Haake Searle-type rotational viscometer (Haake Mess-Technik GmbH u. Co, Germany) were used. All the measurements were carried out either in a shear rate sweep mode or in a constant shear rate mode. A thin layer of silicone oil was deposited upon the upper free surface of the samples in order to prevent evaporation of solvents when measurements were taken at high temperatures, in ambient air, with the Bohlin VOR viscometer.

High-pressure viscometry measurements were performed with a modified Haake Searle-type (concentric cylinder) viscometer. The equipment consisted of a high-pressure vessel capable of maintaining a pressure of up to 1000 bar, which was situated inside an electrically heated metal block, incorporating a basic Haake Searle-type viscometer unit, RV 100. In this viscometer the linkage between the driving motor and the rotor, located inside the pressure vessel, is established by means of permanent magnets. The measurable shear stress range, which is limited by the specific high-pressure fixture and the magnetic coupling strength, was 2.5–60 Pa. The temperature was varied from room temperature ($\sim 20^\circ\text{C}$) to 150°C, and the nominal shear rate varied up to 1130 s^{-1} . A detailed description of the structure and performance of this viscometer may be found in Ref. [13].

The phase separation conditions (see later) of the polymer solutions were determined by monitoring the sharp drop of measured shear stress during the variation of either temperature or pressure with the values of other variables fixed. Detailed descriptions about this method can be obtained from Refs. [8,14,15]. A visual determination was also used to detect the phase separation.

Since the viscosity of an aqueous PVA solution increases gradually during storage, all viscosity measurements of these PVA solutions were carried out five days after preparation of the solution except where it is specifically stated otherwise in the text.

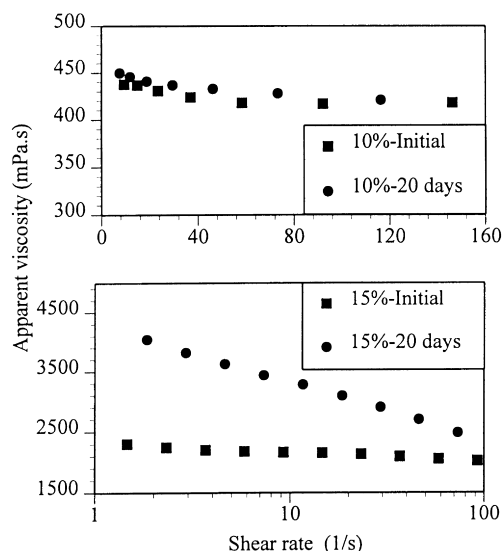


Fig. 1. Apparent viscosity and shear rate interrelationship for two aqueous PVA-72-98 solutions (see Table 1) with different PVA concentration (10 and 15%) at 25°C; data were obtained upon preparation of the solution and after a 20 days interval with the Bohlin viscometer.

3. Results and discussions

3.1. The effects of degree of hydrolysis

It is well documented that the solubility of PVA in water is primarily determined by the degree of hydrolysis [1,2,5,6]. Very high degrees of hydrolysis, 98% or greater, make the polymer highly crystalline and form strong inter and intra chain hydrogen bonding. Thus, the solubility of a PVA decreases significantly with increase of degree of hydrolysis, in particular in the range near 98%. For a highly hydrolysed PVA, 98%, a preparation temperature of above 80°C is required for complete dissolution in water in an

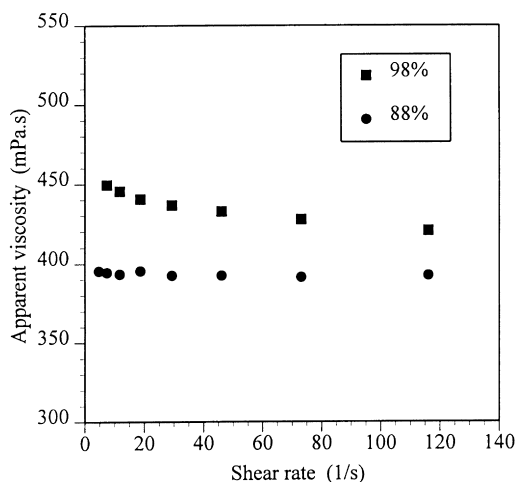


Fig. 2. Apparent viscosity and shear rate interrelationship for a 10% PVA solution with different degrees of hydrolysis, $T = 25^\circ\text{C}$; molecular weights are 72,000 for 98% PVA and 100,000 for 88% PVA, respectively, and data were obtained with the Bohlin viscometer.

acceptable time. It is believed that, for this polymer, inter and intra hydrogen bonding in the PVA chains is disrupted by thermal energy, thus increasing solubility of the PVA. Upon cooling, it is expected that the inter and intra chain hydrogen bonding can re-form. This interaction between chains gradually increases the viscosity of the PVA solutions and a gel structure may be created (a phase separation process) depending upon storage temperature, polymer concentration, and degree of hydrolysis of the PVA [16–18]. Fig. 1 shows the interrelationship between apparent viscosity and shear rate for an aqueous PVA-72-98 solution with two different solute concentrations. It is seen from the figure that the apparent viscosity increases significantly when the polymer concentration increases from 10 to 15%. After 20 days, for the solution with 15% PVA, the apparent viscosity significantly increases and a pronounced shear thinning behaviour is observed compared with those results mentioned previously. For the solution with 10% PVA, the rheological properties remain almost unchanged over the same storage time. This increase of viscosity, for the higher concentration, is most certainly due to the gradual increase of the extents of inter and intra chain hydrogen bonding during the storage period of the solution and hence the increase in interactions and entanglements between the PVA chains. The increase of shear thinning behaviour with age of the solution also indicates the presence of stronger polymer chain associations.

A PVA with a degree of hydrolysis below 88% dissolves in water much more readily at room temperature than one with a higher degree of hydrolysis, and its viscosity shows little change with storage time. The increase in number of hydrophobic acetate groups, i.e. decrease of degree of hydrolysis, disrupts inter and intra chain hydrogen bonding and consequently increases the solubility of the PVA. The decrease of associations between polymer chains also reduces the apparent viscosity of the PVA solution [1,2,5,6]. Fig. 2 shows this effect upon the apparent viscosity of two aqueous (10%) PVA solutions with different degrees of hydrolysis. It is noticed that the solution with a degree of hydrolysis of 98% shows a higher viscosity than the solution with a degree of hydrolysis of 88%, although the molecular weight of the former solution was lower than that of the second solution.

A relatively different result is obtained when comparing the apparent viscosity of PVA solutions with lower degrees of hydrolysis; see Fig. 3. The data in this figure show that the apparent viscosity of the solution with a degree of hydrolysis of 72.5%, PVA-37.5-72.5, is significantly higher than that of the solution with a degree of hydrolysis of 78%, PVA-37.5-78. As was discussed before, the presence of the hydrophobic acetate groups in the PVA chains reduces inter and intra chain hydrogen bonding. As a consequence, the solubility of the PVA is enhanced due to the increase of the degree of hydrogen bonding between the PVA chains and water molecules. An increase of viscosity with increase of interaction between solute and solvent is anticipated.

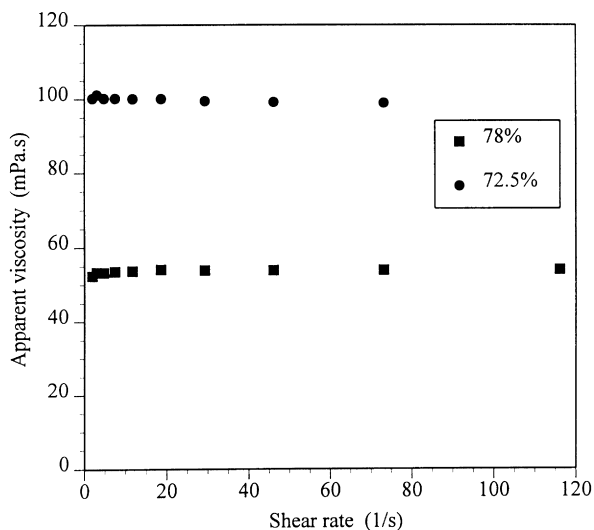


Fig. 3. Apparent viscosity and shear rate interrelationship for a 10% PVA solution with different degrees of hydrolysis, $T = 25^\circ\text{C}$; molecular weight is 37,500 for both polymers, and data were obtained with the Bohlin viscometer.

Based upon the above results, as well as results reported in literature [1,2,5,6], a generalised schematic diagram of the interrelationship between solution viscosity and degree of hydrolysis and also between solubility and degree of hydrolysis for aqueous PVA solutions may be drawn as shown in Fig. 4; the other system variables are fixed. The apparent viscosity shows a decrease with initial decrease of degree of hydrolysis and then an increase with further decrease of degree of hydrolysis. On the contrary, the solubility shows a maximum with variation of extent of hydrolysis. The viscosity and degree of hydrolysis curves are functions of polymer molecular weight, solute concentration, storage time of the solution, and ambient temperature. It is also worth mentioning that the interactions between solute and solvent will also decrease with a further increase of the acetate group fraction in the PVA chains due to the increasingly hydrophobic influence of the additional acetate groups. As a

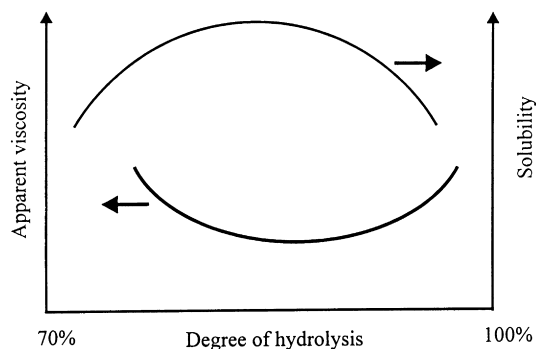


Fig. 4. Schematic diagram of the interrelationship between apparent viscosity and degree of hydrolysis, and between solubility and degree of hydrolysis for aqueous PVA solutions; other conditions are fixed.

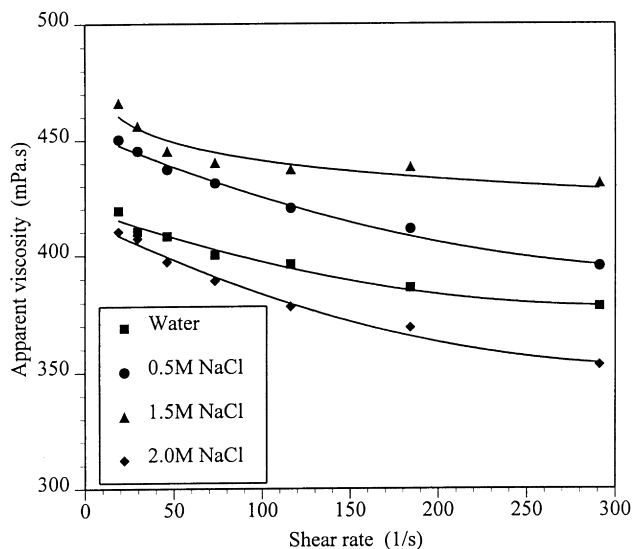


Fig. 5. Apparent viscosity and shear rate interrelationship for 10% PVA-72-98 aqueous solutions containing NaCl, $T = 25^\circ\text{C}$; data were obtained with the Bohlin viscometer.

result of this effect, the PVA now becomes insoluble in water when the degree of hydrolysis falls below ca 70%.

3.2. The effect of electrolyte

The effect of electrolyte upon the nature and extent of hydrogen bonding in pure water and in water soluble polymer systems has been studied extensively [19–21]. It is generally agreed that the addition of electrolytes disrupts the extent of the structure of the hydrogen bonding, reduces the degree of hydrogen bonding in these systems, and causes a decrease of viscosity for both water [21,22] and the corresponding aqueous polymer solutions [8,9]. For aqueous PVA solutions, the situation is rather more complicated

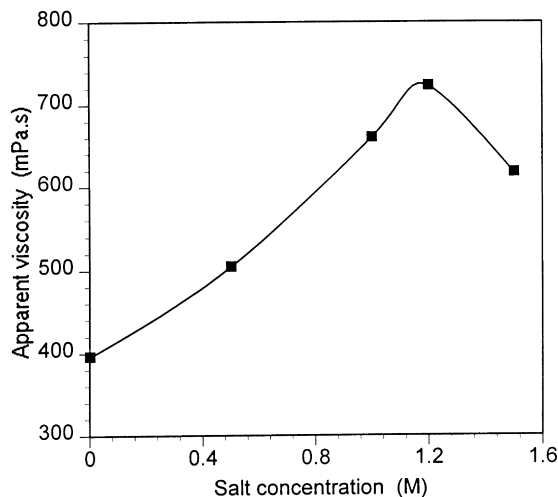


Fig. 6. Effect of salt concentration upon apparent viscosity for a 10% PVA-100-88 aqueous solution, $T = 25^\circ\text{C}$, shear rate = 46 s^{-1} . Data were obtained with the Bohlin viscometer.

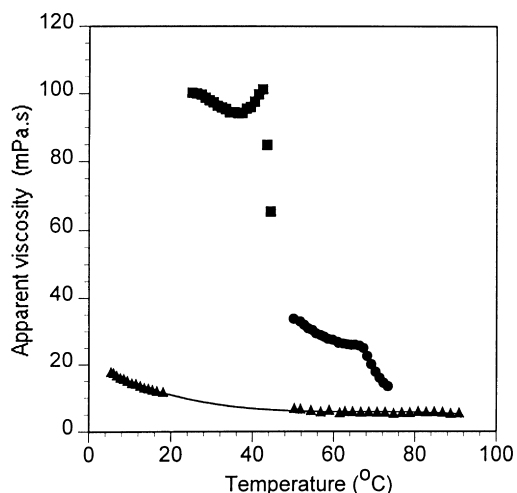


Fig. 7. Effect of temperature upon apparent viscosity for 10% aqueous PVA solutions, shear rate = 1.46 s^{-1} ; data were obtained with the Bohlin viscometer, ■, PVA-37.5-72.5; ●, PVA-37.5-78; ▲, PVA-14-83.

than for many other aqueous polymer solutions due to the existence of hydrogen bonding not only between the PVA chains and water molecules but also within the PVA chains themselves. Thus, it is expected that both kinds of hydrogen bonding will be affected by the addition of electrolytes. Fig. 5 shows the relationship between apparent viscosity and shear rate for a 10% aqueous PVA-72-98 solution of different NaCl concentrations. It is seen from the figure that the viscosity curves of the PVA solutions shift upwards with the initial addition of NaCl up to 1.5 M, and a contrary change of apparent viscosity is observed when the concentration of NaCl in the solution is 2.0 M. In Fig. 6 the apparent viscosity, at a constant shear rate of 46 s^{-1} , for a 10% aqueous PVA-100-88 solution containing different amounts of NaCl is shown. A similar trend to that noted in Fig. 5 is obtained;

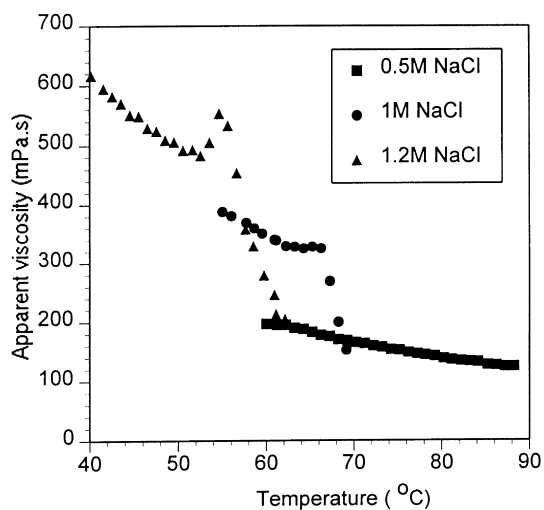


Fig. 8. Effect of temperature upon apparent viscosity for 10% PVA-100-88 in different saline aqueous solutions, shear rate = 1.46 s^{-1} ; data were obtained with the Bohlin viscometer.

i.e. the apparent viscosity attains a maximum at a salt concentration of approximately 1.2 M, then decreases with a further addition of salt.

The experimental results presented in Figs. 5 and 6 indicate that the initial addition of NaCl primarily disrupts the inter and intra chain hydrogen bonding of the PVA chains. As a consequence, the solubility, and by the same effect, the interactions between polymer chains and water molecules now increase. This leads to an increase of the apparent viscosity of the solution. However, with a further increase of salt concentration, hydrogen bonding between solute and solvent is also disrupted, which consequently leads to a decrease of viscosity and the occurrence of the “salting out” effect [2]. This salting out effect is an apparent and natural outcome of the loss of solvency at high salt contents for the PVA. It was found in the current study that aqueous PVA solutions with a degree of hydrolysis of 98% salted out at a NaCl concentration of 3.0 M. The salting out effect is also observed at a salt concentration of ca. 2.0 and ca. 0.6 M for the aqueous PVA-100-88 and PVA-37.5-72.5 solutions, respectively. The decrease of salt content, required to produce the salting out effect, with the decrease of degree of hydrolysis is also consistent with the individual effects of degree of hydrolysis upon intra and inter hydrogen bonding and solvent–solute hydrogen bonding. It can also be concluded that the addition of salt, and the increase of the acetate group fraction in the PVA chains affect the two classes of hydrogen bonding in the solutions in a comparable way. In a study of the effect of electrolyte upon the intrinsic viscosity of aqueous PVA solutions, Maeda et al. have also reported a similar interrelationship between intrinsic viscosity and electrolyte content [12].

3.3. The effect of temperature

The general behaviour of the viscosity–temperature interrelationship for aqueous PVA solutions with high degrees of hydrolysis (above 83%) is similar to that of many polymer solutions that show a decrease of viscosity with an increase of temperature. Fig. 7 describes the viscosity and temperature interrelationship for a 10% PVA-14-83 aqueous solution. Viscosity decreases continuously over the temperature range 5–90°C. However, a different behaviour was observed for 10% aqueous PVA solutions with a degree of hydrolysis lower than 83%; see also Fig. 7. For instance, the viscosity of the PVA-37.5-78 aqueous solution decreased gradually with increase of temperature up to ca. 67°C; then a rather sharp decrease of viscosity occurs at higher temperatures. For the PVA-37.5-72.5 aqueous solution a slight increase of viscosity with increase of temperature was observed above 36°C, and then a very sharp decrease of viscosity was noted with a further increase of temperature above 42°C. This pronounced decrease of viscosity is ascribed to the occurrence of phase separation. A visually detectable precipitation and settlement of PVA was observed upon emptying the viscometer. These results

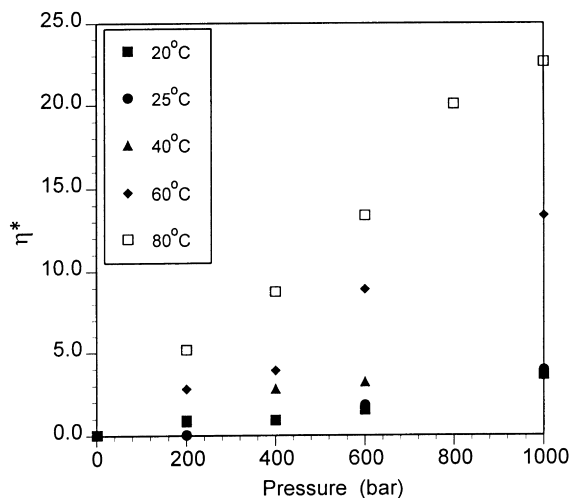


Fig. 9. Interrelationship between relative viscosity difference, η^* (see text), and pressure for a 5% PVA-72-98 aqueous solution at different temperatures, shear rate = 226 s^{-1} . Data were measured with the Haake viscometer.

indicate that the extent of hydrogen bonding between the PVA and water molecules is disrupted at elevated temperatures. The occurrence of phase separation is the obvious result of reduction of water solvency. With the introduction of the more hydrophobic acetate group (lower degree of hydrolysis) into the polymer chains, the phase separation temperature decreases. When the degree of hydrolysis was higher than 83%, no phase separation was observed for any of the aqueous PVA solutions in the closed pressure vessel, at the highest available ambient temperature of 130°C , in the current experiments.

It has been stated earlier that the presence of NaCl in aqueous PVA solutions has an effect of disrupting hydrogen

bonding between both PVA and water molecules, and between the PVA chains themselves. It is expected that a phase separation process may also occur at elevated temperatures for those PVA solutions with high degrees of hydrolysis when inter and intra chain hydrogen bonding is reduced and in turn, solute–solvent hydrogen bonding is increased by the addition of NaCl into the solutions. Fig. 8 provides the viscosity and temperature interrelationships for a 10% solution of PVA-100-88 in water with different salt concentrations. It is noticed that there is no sharp change of viscosity with increase of temperature for the PVA in 0.5 M NaCl aqueous solution in the range of temperature up to 90°C . However, the sharp decreases of viscosity, with increase of temperature, were obtained for the polymer in aqueous solutions with 1 M NaCl. For the PVA in 1.2 M NaCl aqueous solution, a sharp increase of viscosity, followed by a remarkable drop of viscosity, is observed. The temperature corresponding to the sharp decrease of viscosity decreases with increasing salt concentration—that is ca 67°C for 1.0 M NaCl solution and 54°C for 1.2 M NaCl solution, respectively. Again, these rapid decreases of viscosity are caused by phase separation of the polymer in these aqueous salt solutions. The addition of NaCl reduces the extent of hydrogen bonding in the systems and the more significant effect of NaCl addition, modifying the hydrogen bonding between PVA and water molecules at higher salt concentrations, is the reason for the observed phase separation of these solutions.

3.4. The effects of pressure

The study of the influence of pressure upon the rheological properties of PEO solutions has revealed some unexpected results: the viscosity of PEO solutions decreases with increase of pressure, and a sharp decrease of viscosity (corresponding to phase separation) occurs with a further increase of pressure, see Refs. [8,9,23]. This behaviour is naturally associated with the deterioration of solvent quality, due to the break-down of hydrogen bonding between the PEO chains and water molecules, with the increase of pressure. For aqueous PVA solutions in which hydrogen bonding exists not only between PVA chains and water molecules but also within the polymer chains themselves, the application of pressure may be expected to produce effects upon both types of hydrogen bonding and thus give rise to different rheological responses. The variation of the extent of hydrogen bonding, for the inter and intra chain and solute–solvent hydrogen bonding, produced by varying the degree of hydrolysis of the PVA, provides an opportunity to identify the origins of the effects of pressure upon the structure of the solution and the resulting viscosity.

In order to normalise the observed influences of pressure for comparison of the current data (measured at different solute concentrations, polymer molecular weights, temperatures and shear rates) it is useful to choose a relative viscosity difference parameter, $\eta^* = \frac{\eta_p - \eta_1}{\eta_1} \times 100\%$, (where η_1

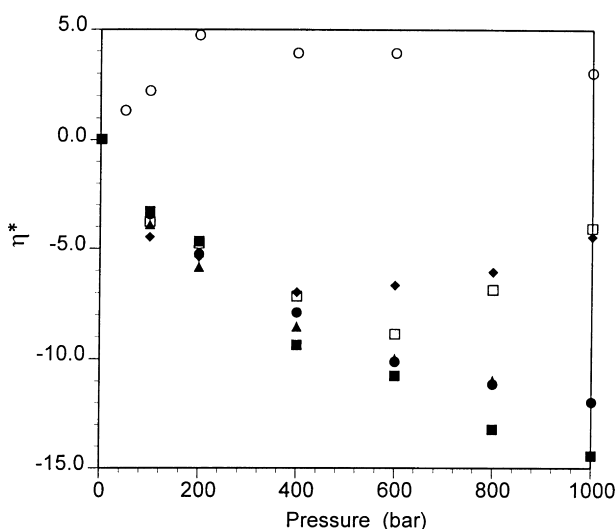


Fig. 10. Interrelationship between relative viscosity difference, η^* , and pressure for a 10% PVA-37.5-78 aqueous solution at different temperatures, shear rate = 226 s^{-1} . Data were measured with the Haake viscometer. ■, 25°C ; ●, 35°C ; ▲, 40°C ; ◆, 60°C ; □, 63°C ; ○, 67°C .

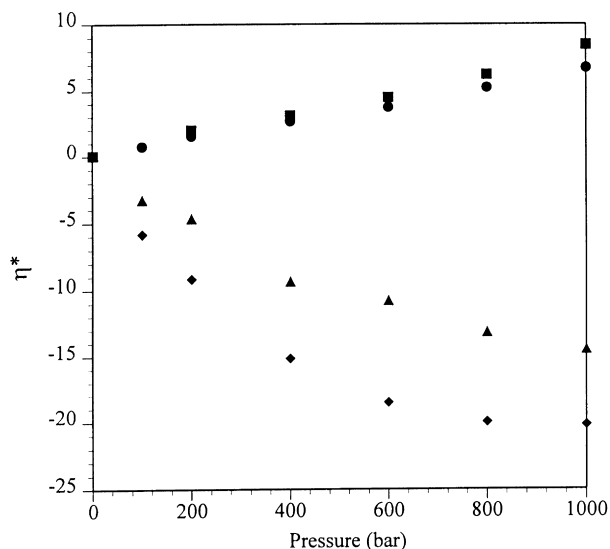


Fig. 11. Interrelationship between the relative viscosity difference, η^* , and pressure for a 10% aqueous PVA solution with different degrees of hydrolysis, $T = 25^\circ\text{C}$, shear rate = 226 s^{-1} . Data were obtained with the Haake viscometer. ■, 10% PVA-100-88; ●, 10% PVA-14-83; ▲, 10% PVA-37.5-78; ◆, 10% PVA-37.5-72.5.

and η_p are the apparent viscosities at pressures of 1 and P bar, respectively). The interrelationship between the relative viscosity difference, η^* , and pressure for a 5% PVA-72-98 aqueous solution, at different temperatures, is given in Fig. 9. It is observed that the value of η^* increases with increase of pressure at temperatures between 20 and 80°C , and that it also increases with increase of temperature.

However, a rather different behaviour was observed for the PVA-37.5-78 aqueous solutions; see Fig. 10 where the relationship between the relative viscosity difference, η^* , and pressure for these solutions at different temperatures is shown. It is seen from the figure that the value of η^*

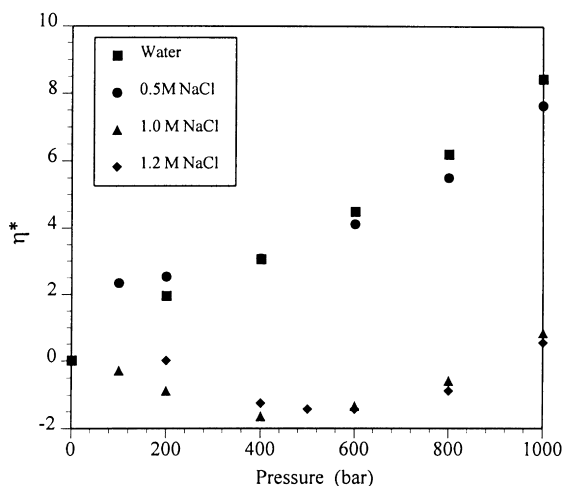


Fig. 12. Interrelationship between the relative viscosity difference, η^* , and pressure for a 10% PVA-100-88 aqueous solution with different saline concentrations, $T = 25^\circ\text{C}$, shear rate = 226 s^{-1} . Data were obtained with the Haake viscometer.

decreases continuously with increase of pressure up to 1000 bar at temperatures below 40°C . At temperatures between 40 and 63°C , an initial reduction of the value of η^* is observed, followed by an increase of the value of η^* with further increase of pressure. At a temperature of 67°C , the value of η^* now increases with increase of pressure. It should be recalled that a phase separation occurs at 1 bar at this temperature and more results will be discussed later concerning the effect of pressure upon viscosity around the phase separation temperature for these PVA solutions. This variation of η^* with pressure at temperatures below the phase separation temperature is qualitatively similar to that of PEO in both pure water and in electrolyte aqueous solutions [8,9]. Similar phenomena were also observed for an aqueous 10% PVA-37.5-72.5 solution where the crossover of η^* occurs at 42°C .

To compare the effects of degree of hydrolysis upon the value of η^* induced by the application of pressure, the value of η^* at 25°C is plotted against the applied pressure in Fig. 11 for aqueous PVA solutions with degrees of hydrolysis of 88, 83, 78 and 72.5%, respectively. It is clear from the figure that the value of η^* increases with the application of pressure when the degree of hydrolysis is higher than 83%, but decreases when the degree of hydrolysis is lower than 78% (increase in absolute value). It is also noticed that the value of η^* decreases with decrease of degree of hydrolysis of the PVA, and that negative values of η^* are computed at the lower degrees of hydrolysis.

The experimental results presented in previous publications have identified that the application of hydrostatic pressure may induce two rather different types of effects upon the viscosity of PEO aqueous solutions [8,9,23]. The first one is simple volumetric compression of the system which leads to an increase of viscosity; the second one is disruption of the overall hydrogen bonding between the PEO chains and water molecules, which causes a reduction of viscosity. Both are potentially important factors in the present PVA systems. However, in PVA solutions the hydrogen bonding structure phenomena are potentially more complicated than those which may exist in PEO solutions. There is now hydrogen bonding not only between the PVA chains and water molecules but it also occurs in the various inter and intra polymer chain interactions in the solution. It is rational to expect that this inter and intra polymer chain hydrogen bonding is also disrupted with the application of pressure. This effect is qualitatively equivalent to that of the progressive introduction of more acetate groups within the PVA chains (e.g. a decrease of degree of hydrolysis), or the addition of salts to aqueous solutions. From the previous discussion, it is recognised that the viscosity of the PVA solutions may be increased by the above changes. Therefore, there is now a third effect (the decrease of intra and inter chain interactions) which may contribute to the increase of viscosity of aqueous PVA solutions at elevated pressures. As a consequence of the combination of these three effects, at higher degrees of hydrolysis, application of pressure leads

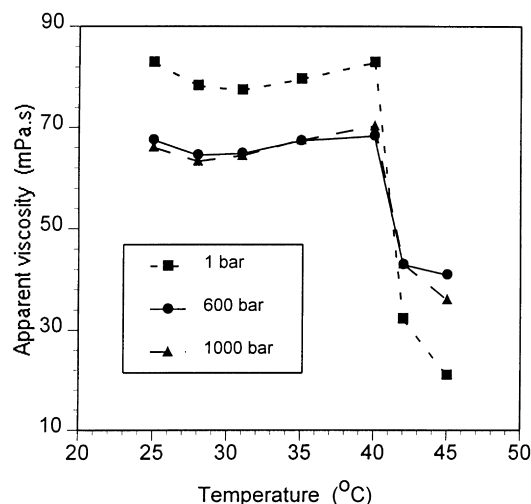


Fig. 13. Viscosity–temperature–pressure interrelationship for a 10% PVA-37.5-72.5 aqueous solution, shear rate = 226 s^{-1} . Data were obtained with the Haake viscometer.

to an increase of viscosity since the extent of inter and intra chain hydrogen bonding is very pronounced. At low degrees of hydrolysis, the extent of inter and intra chain hydrogen bonding decreases, which attenuates the influence of the third effect. On the other hand, the extent of hydrogen bonding between the PVA chains and water molecules increases with decrease of degree of hydrolysis, which causes a more significant effect of pressure in disrupting the hydrogen bonding between solute and water. Thus, a reduction of viscosity with increase of pressure is observed at lower degrees of hydrolysis.

The results presented previously, regarding the effects of salts, showed that the viscosity of aqueous PVA solutions changes with the addition of NaCl, and NaCl content; see Figs. 5 and 6. The changes of viscosity were related to the variation, induced by the presence of salt, of strength of hydrogen bonding existing both within the polymer chains and between solute and solvent. Thus, the effects of pressure upon viscosity are also expected to change with the variation of salt concentration. This is confirmed in Fig. 12 where the influence of pressure upon relative viscosity difference, η^* , for a 10% PVA-100-88 in aqueous solution with different saline concentrations at 25°C is given. A similar trend to that of Fig. 11 is observed in Fig. 12. It is clear that, with the increase of pressure, the value of η^* increases in the saline concentration range lower than 0.5 M and decreases when the saline concentration is above 1 M. It is also seen that a negative value and minimum value of η^* occurs at the higher saline concentrations with increase of pressure.

The effect of salt introduction, upon the pressure and η^* parameter interrelationship, can be interpreted in a similar way to that adopted above. The addition of NaCl in the solution leads to a reduction of inter and intra chain hydrogen bonding. Thus, the influence of pressure upon hydrogen bonding between the polymer chains and water molecules is now more significant than the influence upon hydrogen

bonding within the polymer chains. As a consequence, viscosity decreases with increase of pressure at higher salt concentrations. It should be mentioned that the effect of salt in disrupting the hydrogen bonding between the polymer chains and water molecules still exists in the above cases. A phase separation at higher temperatures or at higher salt concentrations (a salting out) is evident.

The results presented above indicate that the influence of pressure upon the viscosity of aqueous PVA solutions depends upon the extent of hydrogen bonding between the PVA chains and water molecules as well as from inter and intra chain interactions. These data further emphasise the various roles of hydrogen bonding in determining the rheological properties of aqueous PVA solutions; degree of hydrolysis of PVA, presence of electrolytes, temperature and pressure are the variables which change the extent of hydrogen bonding in comparable ways.

3.5. The effect of pressure upon viscosity at the phase separation temperature range

It has been observed in previous studies that for aqueous PEO solutions containing salt, a marked decrease of viscosity occurs during increase of either temperature or pressure [8]. This sharp drop of viscosity is due to the occurrence of phase separation for the PEO solutions caused by disruption of solute–solvent hydrogen bonding, induced by the application of pressure and temperature. Earlier in Section 3.3, the phase separation process, detected rheologically, for PVA solutions, with increase of temperatures was also noted at ambient pressure; see Figs. 7 and 8. Thus it is of interest to study the effect of pressure upon viscosity around the temperature of phase separation for these PVA solutions.

For those aqueous PVA solutions with high degrees of hydrolysis, 98, 88 and 83%, which only exhibit phase separation at lower temperatures [16–18] rather than at elevated temperatures, viscosity increases simply and reversibly with increase of pressure in the temperature range 20–130°C. There are no viscosity discontinuities at pressures up to 1000 bar within this temperature range. The viscosity, after lowering temperature and pressure, remains the same as that observed before the initial increase in temperature and pressure. These results suggest that there is no phase separation at elevated temperatures even with the application of pressure for this type of polymer solution.

For the lower degree of hydrolysis polymer, PVA-37.5-72.5, the viscosity–temperature–pressure relationship in water is given in Fig. 13. Viscosity, at 1 bar, decreases with increase of temperature up to 35°C; then a slight increase of viscosity with further increase of temperature is noticed. However, when the temperature varies from 40 to 42°C, a sharp decrease of viscosity is observed. This phenomenon was also noted using the Bohlin viscometer; see Fig. 7. This indicates the occurrence of a phase separation for the polymer solution in the temperature range 40–42°C

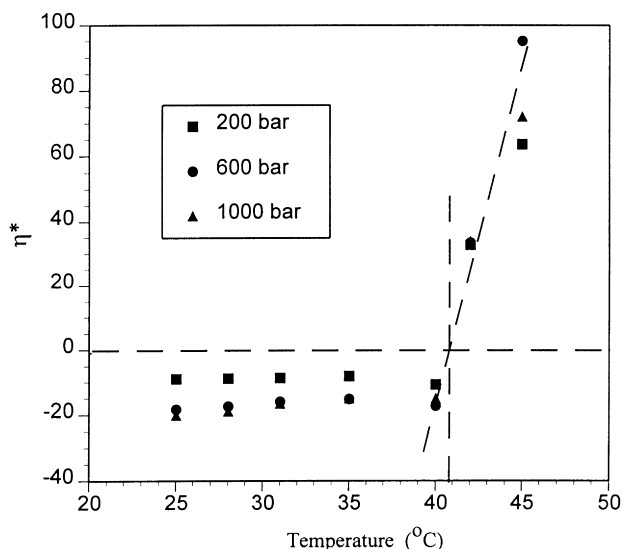


Fig. 14. Temperature and relative viscosity difference, η^* , interrelationship for a 10% PVA-37.5-72.5 aqueous solution at different pressures, shear rate = 226 s^{-1} . Data were measured with the Haake viscometer.

at ambient pressure. At elevated pressures of 600 and 1000 bar, the viscosity varies in a similar way to that at 1 bar with increase of temperature. However, the absolute value is substantially lower than that at 1 bar at temperatures up to 40°C . When the temperature is above 40°C , a sharp decrease of viscosity is again observed, but its subsequent value is significantly higher than that observed at 1 bar. In summary, the application of pressure decreases viscosity of the solution before the phase separation temperature and increases viscosity after that temperature. However, the phase separation temperature itself remains unchanged, within the precision of the experiment, at various pressures. In order to further clarify the effects of pressure upon the viscosity of these solutions, the temperature and relative viscosity difference parameter, η^* , interrelationships, at different pressures, are plotted in Fig. 14. It is seen that, when pressure increases, the relative viscosity difference is negative below the phase transmission temperature and becomes positive above that temperature. Similar behaviour was also obtained for the other three PVA solutions in which phase separation occurs at elevated temperatures.

The phase and rheological behaviour of these PVA solutions, at elevated pressures, is rather different to that shown by aqueous PEO solutions. For PEO solutions, the increase of pressure causes deterioration in solvent quality by disrupting hydrogen bonding between the PEO segments and water molecules. Hence, the phase separation temperature decreases with increase of pressure and consequently the temperature at which a sharp decrease of viscosity occurs also decreases with increase of pressure. For PVA solutions, as was discussed before, hydrogen bonding exists not only between the polymer segments and water molecules, but also between the polymer segments themselves. It has also been indicated by the previous data that the

application of pressure influences the extent of these two types of hydrogen bonding in PVA solutions. It can be appreciated why the phase separation temperature does not decrease with increase of pressure, since the interactions between solvent and solute, and between the PVA segments, may both decrease with increase of pressure. On the contrary, it might be speculated that increase of pressure should increase the phase separation temperature for PVA solutions, since the application of pressure, after the occurrence of phase separation at 1 bar, significantly increases solution viscosity. This result may indicate that the application of pressure, above the phase separation temperature, improves the solvent quality. As a consequence, the separated solute becomes soluble and thus solution viscosity now increases with increase of pressure.

The irreversible change of viscosity, at temperatures above the phase separation temperature, with the variation of pressure also provides evidence to support the above ideas. The viscosity of the PVA solution, at temperatures above the phase separation temperature, increases significantly with the increase of pressure, but only decreases partially and slowly when the pressure is decreased to ambient. In contrast, the viscosity recovers fully and rapidly during the variation of pressure at temperatures below the phase separation temperature. This phenomenon also suggests that solubility of the separated PVA solutions increases with the application of pressure since: (1) viscosity increases and (2) the processes of simple compression and decompression of the liquids are reversible and much faster than those of precipitation and dissolution of the polymer in the solvent. Further study concerning this issue is to be carried out and will be reported elsewhere.

4. Conclusions

The rheological properties of aqueous PVA solutions, investigated in this study, are mainly determined by the equilibrium configurations of hydrogen bonding within the polymer chains and between the polymer chains and water molecules. This equilibrium can be varied by changing the degree of hydrolysis of the polymer, adding an electrolyte into the solution, and by varying temperature and pressure in a limited range. At high degrees of hydrolysis, where inter and intra chain hydrogen bonding is dominant in the solutions, the PVA solutions show a pronounced shear thinning behaviour and apparent viscosity progressively increases with storage time due to the formation of strong chain entanglements and associations. The extent of these phenomena decreases steadily with decrease of solute content and degree of hydrolysis. For this case apparent viscosity simply decreases with increase of temperature and increases with increase of pressure.

At lower degrees of hydrolysis, where hydrogen bonding between the PVA chains and water molecules is more significant, viscosity of the PVA solutions decreases with

increase of temperature and pressure due to the disruption of the hydrogen bonding between solute and solvent. A sharp decrease of viscosity, caused by a phase separation process, occurs at elevated temperatures. At those temperatures above the phase separation temperature, the application of pressure enhances the viscosity of the separated solutions, which suggests an increase of solubility induced by pressure in those temperature ranges.

The addition of NaCl initially disrupts inter and intra chain hydrogen bonding and thus increases the solubility of the PVA solutions. The apparent viscosity also increases with the addition of NaCl. However, in high salt concentrations, hydrogen bonding between the solute and the solvent is also reduced and thus the viscosity value of the solutions decreases. A salting out effect is observed at sufficiently high salt concentrations. Generally, the nature of the effect of salt is similar to that which arises from the decrease of degree of hydrolysis. Thus, the effect of temperature and pressure upon the viscosity of PVA solutions also changes with the variation of salt concentration in the solutions.

These experimental results further demonstrate the inter-relationships between the rheological properties and hydrogen bonding in aqueous polymer solutions and the rather equivalent influences of temperature, pressure, and presence of electrolytes in the disruption of the various hydrogen bonding linkages in aqueous polymer solutions. For the PVA system, the degree of polymer chain hydrolysis is also influential and the change of this variable also induces comparable effects to those of temperature, pressure and solvent ionic strength.

Acknowledgements

The authors would like to thank SBFSS for the financial

support to S. Zhu, Schlumberger Cambridge Research for donating the Haake viscometer, and Harco Chemicals, UK, for provision of the PVA samples.

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