Viscosity behaviour of weakly charged polymer–ion complexes comprising poly(vinyl alcohol) and Congo red

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The reduced viscosity, η_R, of poly(vinyl alcohol)–Congo red (PVA–CR) complexes in aqueous solution has some unique features, such as (1) an appearance of a maximum at a given PVA concentration (C_{PVA}) and (2) a time evolution of η_R, but only in the regime where the maximum appears. These characteristic features of the viscosity behaviour are simulated by using the theory of Rice and Kirkwood which takes into account the electrostatic interaction in the reduced viscosity.

(Keywords: poly(vinyl alcohol); viscosity; polymer–ion complex)

INTRODUCTION

Polymer–ion complexes have attracted wide interest due to their scientific and technological importance[1,2]. Most of these complexes can be easily formed by adding different types of ions to an aqueous polymer solution. For example, poly(vinyl alcohol) (PVA) is known as a polymer which is capable of complexation with borate ions[3–9], cupric ions[10], and various other inorganic species, such as titanate[11], antimonate[12], and vanadate[13,14] ions. The complexation process can be classified by two steps, namely mono-complexation and di-complexation. The mono-complexation stage, an attaching of an ion to a unit of a polymer chain, leads to a polyelectrolyte-type behaviour of the polymer chain. When another monomer unit of a polymer chain is complexed to the attached ion, di-complexation occurs and the complexed ion behaves as a crosslink. However, these complexations take place according to a delicate balance of the complexation equilibria. Therefore, the charged groups can be easily dissociated from the polymer chain by changing the ionic environment, resulting in a drastic change in the rheological properties of the polymer solution. For these reasons, these polymer–ion complexes exhibit various features in their rheological properties.

In a previous paper[15], we reported a unique phase behaviour of the PVA–Congo red ion complexes, i.e. a re-entrant sol–gel–sol–gel transition, and discussed the origin of this behaviour. Congo red is a crosslinker of PVA aqueous solutions under either neutral or mild basic conditions. The viscosity of PVA–Congo red aqueous solutions had certain characteristic features, such as (1) an appearance of a maximum at a given PVA concentration (C_{PVA}) and (2) a time evolution of η_R, but only in the limited regime where the maximum appears. These phenomena were qualitatively explained using a model of intra- and intermolecular crosslink formation in conjunction with electrostatic interactions. This model was examined by analysing the structure factor for PVA–Congo red ion complexes, obtained by small-angle neutron and X-ray scattering, as functions of the PVA and CR concentrations[16].

In this paper, we construct a viscosity function based on a theory which takes account of the electrostatic interaction, and discuss the role of attached ions on the viscosity behaviour, as well as the sol–gel phase behaviour in PVA–CR ion complex solutions.

EXPERIMENTAL

Materials

Resaponified poly(vinyl alcohol), having a viscosity-average degree of polymerization (DP) = 1800, was supplied by Nippon Synthetic Chemical Industry Co. Ltd. Details of the sample characteristics are described elsewhere[15]. PVA and Congo red (CR) aqueous solutions were prepared by dissolving each component in deionized water. The required PVA and CR solutions were then mixed at 80°C and kept in a temperature controlled room at 20°C. PVA–borate complex solutions were also prepared in order to compare the rheological properties of the PVA–CR and PVA–borate complex systems. The PVA–borate complex was prepared by mixing PVA, boric acid and NaOH, where NaOH was added to ionize the boric acid[6–8]. The concentration of the NaOH solution was 0.167 M.

Viscosity measurements

The viscosities of PVA–CR complex solutions were measured with a Ubbelohde capillary viscometer at 60 ± 0.05°C. The time required for the solution to pass

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the two menisci of the viscometer was recorded. A typical time taken for this was ~100 s, and was very reproducible, with an error of ±0.1 s in most of the cases. Therefore, the relative error was estimated to be ~0.1%. The measurements were repeated at least three times and the times obtained were arithmetically averaged and then converted to the relative viscosity, η_{rel}, i.e. the ratio of the solution viscosity, η, and that of the solvent, η_0. Most of the experiments were carried out by diluting the polymer solution step by step, which is a typical procedure adopted in Ubbelohde capillary viscometry. In some cases, however, a viscosity thickening was observed during the repetition of the viscosity measurement. In such a case, each polymer solution was individually examined after ageing the solution in the Ubbelohde capillary viscometer at 60°C.

The relative viscosity, η_{rel}, was further converted to the reduced viscosity, η_R, via the specific viscosity η_{sp}, both of which are defined as follows:

$$\eta_{sp} = \eta_{rel} - 1 \qquad (1)$$

and

$$\eta_R = \frac{\eta_{sp}}{C_{PVA}} \qquad (2)$$

where C_{PVA} is the PVA concentration in monomeric units. Thus the intrinsic viscosity, $[\eta]$, can be described by the following:

$$\eta_R \rightarrow [\eta], \quad \text{for } C_{PVA} \rightarrow 0 \qquad (3)$$

RESULTS

Electrostatic screening effects on viscosity

Figure 1 shows the variation of the reduced viscosity, η_R, for PVA aqueous solutions of PVA–CR and PVA–borate ion complexes. The abscissa is the crosslinker concentration, C_x, i.e. the CR or boric acid concentration. The PVA concentrations used were 0.12 and 0.11 mol l^{-1}, respectively, for the PVA–CR and PVA–borate complexes. Although these concentrations are smaller than the calculated chain overlap concentration, $C^*_{PVA} \sim 0.55$ mol l^{-1} (ref. 15), it should be pointed out that we are examining here the crossover region from the dilute to the semidilute regimes because of the fact that the PVA chains are expected to be highly expanded owing to the attached ions. It should be noted that η_R for the PVA–CR ion complex is a stronger function of C_x than that of the PVA–borate complexes. In particular, for $C_x > 0.012$ mol l^{-1}, a steep increase in η_R for the PVA–CR system is observed, which is in contrast to the C_x dependence of the PVA–borate complexes. We will discuss this point later.

PVA concentration dependence

Figure 2 shows the variation of η_R as a function of C_{PVA} for various CR concentrations. In the case of $C_{CR} = 0$, η_R behaves just as would be expected for a neutral polymer solution. The ordinate is taken with a logarithmic scale so as to stress the change in η_R at low C_{CR} values. By adding CR, η_R shows an upturn at low C_{PVA} values, typical of polyelectrolytes[17,18]. The higher the C_{CR}, then the higher the η_R at low C_{PVA} values. This clearly indicates that the higher the C_{CR}, then the higher is the concentration of the PVA–CR complexes. For $C_{CR} \leqslant 0.003$ mol l^{-1}, most of the added CR ions seem to be attached to PVA chains and generate a repulsive interaction between the latter, where no significant electrostatic screening effect is observed in this concentration range. This kind of polyelectrolyte effect, an upturn behaviour in η_R at low C_x values, was not observed for the PVA–borate complexes, as shown in Figure 3 of ref. 8.

For larger C_{CR} values (i.e. $C_{CR} \geqslant 0.015$ mol l^{-1}), η_R starts to show a distinct maximum with increasing C_{CR} over the intermediate concentration range of PVA, i.e. 0.05 mol l$^{-1} \leqslant C_{PVA} \leqslant 0.4$ mol l^{-1}. A time-dependent viscosity thickening was also observed exclusively in this concentration regime. The plots shown here are corresponding to equilibrium values of η_R, which were measured 4 days after loading the solution into the viscometer. For $C_{PVA} > 0.4$ mol l^{-1}, however, η_R becomes insensitive to either C_{CR} or time, and the viscosity varies similarly to that of a PVA aqueous solution, i.e. $C_{CR} = 0$. The maximum value of η_R is about 10 to 40 times as high as that for the case with $C_{CR} = 0$, when compared at the same C_{PVA} value. It is worthwhile to note that the PVA concentration where η_R recovers a behaviour which is similar to that of the non-charged PVA solution, is roughly proportional to C_{CR}.

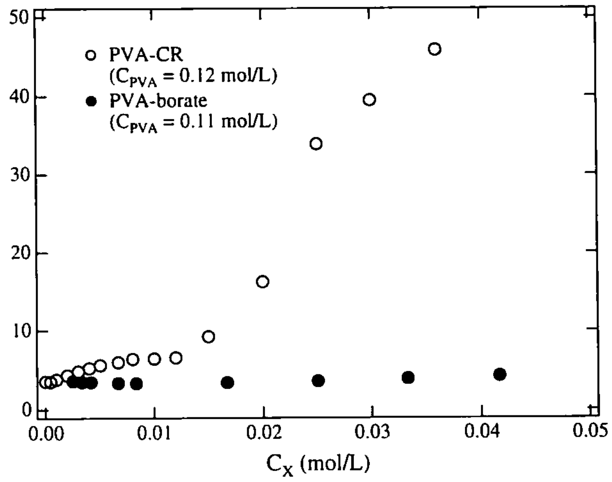

Figure 1 Crosslinker concentration (C_x) dependence of the reduced viscosity, η_R: (●) boric acid; (○) Congo red

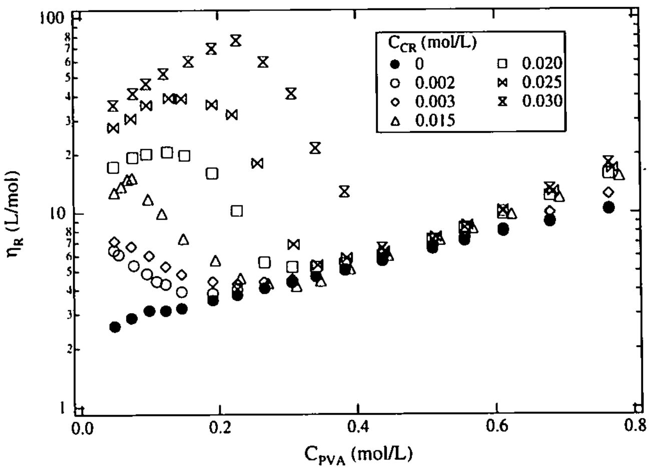

Figure 2 C_{PVA} dependence of η_R for various concentrations of Congo red (CR)

DISCUSSION

In this section, we shall try to explain the unique viscosity behaviour of the PVA–CR aqueous solutions described above. CR molecules dissociate into CR ions (abbreviated to CR^{2-}) and Na^+ ions in an aqueous solution as follows:

$$CR \leftrightarrow CR^{2-} + 2Na^+$$

We assume here a 100% dissociation of the CR molecules under the conditions employed in this work. This assumption is supported by the fact that direct dyes, e.g. Congo red, are highly dissociated in aqueous solutions[19]. Therefore, the CR ion concentration, $[CR^{2-}]$ can be regarded as being equal to C_{CR} without losing the essential points of the discussion.

Electrostatic screening effects on viscosity

As was shown in *Figure 1*, a significant difference in the viscosity behaviours was observed between the PVA–borate and PVA–CR complexes at $C_x > 0.015 \text{ mol l}^{-1}$. Let us clarify the reason for this.

Figure 3 shows enlarged plots of *Figure 1*, where it should be noted that the ordinate is highly expanded. The slight discrepancy in the limiting value of η_R at $C_x = 0$ is due to the presence of NaOH in the PVA–borate complexes. As shown in this figure, η_R for the PVA–borate complexes at first slightly decreases, and then increases with C_x. This interesting behaviour was also observed by Ochiai *et al.*[4] for the intrinsic viscosity, $[\eta]$, of PVA–borax aqueous solutions. According to the theory of Leibler *et al.*[20], the initial concentration in $[\eta]$ is due to the intrachain crosslinking via complexation of the PVA–borate ions. This kind of contraction was observed when a small amount of salt was added to the solution. The subsequent increase in $[\eta]$ with increasing C_x was explained as being due to an electrostatic repulsion between the attached ions on the PVA chains. However, such a type of variation in η_R or $[\eta]$, i.e. a contraction and a gradual increase in η_R, was not observed for the PVA–CR system. The absence of a contraction in $[\eta]$ at low C_x values for PVA–CR is explained as follows. Since there is no added salt in the case of PVA–CR, the addition of a small amount of CR ions leads to an expansion of the PVA chains. In the case of the PVA–borate complexes, the electrostatic repulsion between the attached ions is highly screened by the Na^+ and OH^- ions introduced in order to ionize the boric acid. These ions behave as an added salt.

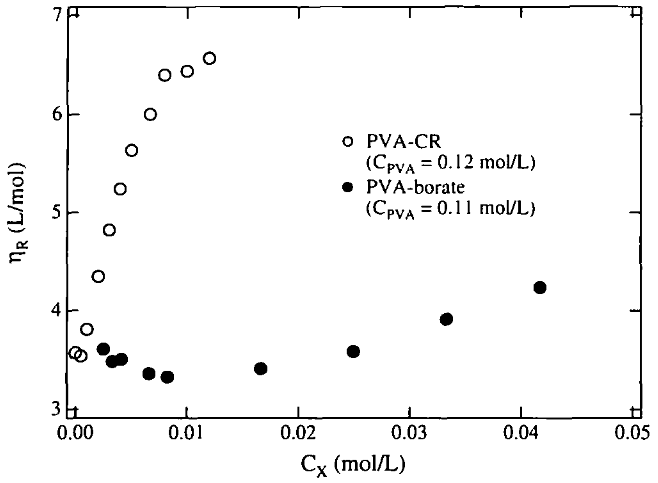

Figure 3 Crosslinker concentration, C_x, dependence of the reduced viscosity, η_R, at low C_x levels: (●) boric acid; (○) Congo red

The spatial range of the electrostatic screening is given by the so-called Debye screening length, r_D, which is a function of the ionic strength, I, and the Bjerrum length, Q, as follows:

$$r_D = (8\pi N_A Q I)^{-0.5} \tag{4}$$

where

$$I = \frac{1}{2}\sum_i C_i z_i^2 \tag{5}$$

and

$$Q = \frac{e^2}{4\pi\varepsilon k_B T} \tag{6}$$

where C_i and z_i are, respectively, the concentration and valency of the ion i. N_A, e, ε, and $k_B T$, are the Avogadro constant, the elementary charge, the dielectric constant, and the Boltzmann energy, respectively. The value of r_D for the solution with borate ion ($C_x = 0.01 \text{ mol l}^{-1}$) and NaOH (0.167 M) is calculated to be 7.3 Å at 25°C. On the other hand, r_D for the CR solution with $C_x = 0.01 \text{ mol l}^{-1}$ is 18 Å; note that z is 2 for CR ions. Although these values are modified by complexation with PVA when these molecules are present in the solution, the estimated difference in r_D seems to be significant enough to change the viscosity behaviour at low C_x values (see *Figure 3*), which is ascribed to the addition of NaOH to the borate solution.

The steep increase in η_R for $C_{CR} > 0.012 \text{ mol l}^{-1}$ in *Figure 1* can be explained by using the same reasoning. When the number of attached CR ions is increased by increasing C_x, the repulsive electrostatic interaction increases as the quadratic power of C_x, according to the Coulomb law. In reality, the distance between charges should decrease with C_x because of a further attachment of CR ions to the PVA chains, thus giving rise to a higher power of C_x in the electrostatic potential. This may be the case for PVA–CR at $C_x > 0.012 \text{ mol l}^{-1}$. In the case of the PVA–borate ion complex with NaOH (0.167 M), the concentrations of Na^+ and OH^- are of the order of $10^{-1} \text{ mol l}^{-1}$, which are at least ten times as high as the borate concentration. The experimental evidence shown above clearly indicates that the electrostatic interaction plays an important role in generating the unique rheological properties of the PVA–CR aqueous solutions.

PVA concentration dependence

It is well known that the reduced viscosity, η_R, for polyelectrolyte solutions is considerably different from that of neutral polymer solutions at low polymer concentrations. This is empirically described by Fuoss[17,18] as follows:

$$\eta_R = \frac{A}{1 + BC^{0.5}} \tag{7}$$

where A and B are constants and C is the polymer concentration. Since equation (7) does not have any fundamental theoretical basis, theoretical investigations have been made by several workers, such as, Witten and Pincus[21], Rabin[22], Borsali *et al.*[23], and Nishida *et al.*[24].

These theories predict that η_R has a maximum, $\eta_{R,max}$ at C_{max}, in the plot of η_R *versus* C, and that $\eta_{R,max}$ becomes higher and C_{max} moves to a lower concentration by increasing the charge density on the polymer or by decreasing the salt concentration[23]. Our results for the C_x dependence of $\eta_{R,max}$ are opposite to that predicted by the theories, i.e. $\eta_{R,max}$ moves to a larger C_{PVA} with increasing C_{CR}. This contradiction may be accounted for by the ion complexation equilibrium between PVA and CR.

Now we shall try to reproduce the η_R variation as a function of C_{PVA}, based on the Rice and Kirkwood (RK) theory[25]. Although the RK theory itself does not take account of the polymer effect, it provides a clear physical picture of the electrostatic interaction between charges when compared with more sophisticated theories[21–23]. Therefore, we will use the RK theory, as employed by Nishida *et al.*[24], so as to stress the contribution of the electrostatic interaction of the attached charges on a polymer chain. The polymer effect will be incorporated by introducing the radial distribution function of the attached ions for a charged polymer chain. According to the theory, the contribution of the electrostatic interaction between charges to the reduced viscosity, $\eta_{R,ion}$, is given by the following:

$$\eta_{R,ion} \approx C^2 \int_{r_0}^{\infty} r^2 \left[u''(r) + \frac{4u'(r)}{r} \right] g(r) 4\pi r^2 \, dr \qquad (8)$$

where r_0 is the lower cutoff and $u'(r)$ and $u''(r)$ are the first and second derivatives, respectively, of the electrostatic potential, $u(r)$, which is itself given by the following[20]:

$$\frac{u(r)}{k_B T} = \frac{(ze)^2}{4\pi\varepsilon r k_B T} \exp\left(-\frac{r}{r_D} \right) = \frac{z^2 Q}{r} \exp\left(-\frac{r}{r_D} \right) \qquad (9)$$

where z is the valence number of the polyion, and r_D is the Debye length, as defined in equation (4). In addition, $g(r)$ is the radial distribution function of the polyion and is given for a dilute polymer solution as follows[26]:

$$g(r) = \exp\left(-\frac{u(r)}{k_B T} \right) \qquad (10)$$

When $u(r) \ll k_B T$, equation (10) can be truncated to:

$$g(r) \approx 1 - \frac{u(r)}{k_B T} \qquad (11)$$

This enables one to perform the analytical integration of equation (8), which gives the following:

$$\eta_{R,ion} \approx C^2 \left[z^2 Q \left(\frac{r_0^3}{r_D} + r_0^2 \right) \exp\left(-\frac{r_0}{r_D} \right) + z^4 Q^2 \left(-\frac{r_0^2}{2r_D} + \frac{r_0}{2} + \frac{5r_D}{4} \right) \exp\left(-\frac{2r_0}{r_D} \right) \right] \qquad (12)$$

The assumption made in the derivation of equation (12) was confirmed as being relevant as long as we set an appropriate value for r_0 in the process of the integration of equation (8). So now we can estimate r_0, the distance between the neighbouring charges on the chain, based on the discussion by Leibler *et al.* for PVA–borate ion complexes[20]. Thus, r_0 is given by the following:

$$r_0 = b_{PVA} \sqrt{n} \qquad (13)$$

where $b_{PVA}(=6.3\ \text{Å})^{27}$ is the segment length of the PVA chain and n is the number of monomers between successive attached ions on a chain. The latter is given by:

$$n = \frac{1 + \tilde{K} C'_{CR}}{\tilde{K} C'_{CR}} \qquad (14)$$

where $\tilde{K}$ is the effective complexation constant, given as follows:

$$\tilde{K} = K \exp\left(-\frac{\alpha u(r=r_0)}{k_B T} \right) \qquad (15)$$

This implies that the effective complexation constant is suppressed by the presence of an electrostatic potential. In equation (15), α is a numerical factor, which is fixed at 4^{20}, $u(r=r_0)$ is the electrostatic interaction energy between charges separated by r_0, and C'_{CR} is the concentration of free CR ions. Since C'_{CR} is a decreasing function of C_{PVA}, we assume the following functional forms for C'_{CR}:

$$C'_{CR} = C_{CR} - \frac{1}{20} C_{PVA}, \quad \text{for } C_{CR} > \frac{C_{PVA}}{20} \qquad (16a)$$

and

$$C'_{CR} = 0, \quad \text{for } C_{CR} \leqslant \frac{C_{PVA}}{20} \qquad (16b)$$

The numerical factor, 1/20, is based on the results obtained by Fujino and Fujimoto[28]. This indicates that CR molecules are attached to every 20 monomer units of the PVA chains, at most. The complexation constant, K, in the absence of any electrostatic interaction, is estimated to be 11 l mol^{-1} for PVA–borate ion complexes[20]. We shall employ this value here in order to simulate the reduced viscosity variation with C_{PVA}.

The variations of $\eta_{R,ion}$ *versus* C_{PVA}, for $C_{CR} = 0.015$, 0.020, 0.025, and 0.030 mol l^{-1} are shown in *Figure 4*. The general trend of $\eta_{R,ion}$ well reproduces the observed reduced viscosity curves for $C_{PVA} \leqslant 0.4\ \text{mol l}^{-1}$, which indicates that η_{ion} contributes significantly to the net viscosity. In fact, $\eta_{R,ion}$ does have a maximum at around $C_{PVA} = 0.02\ \text{mol l}^{-1}$, which shifts to higher concentrations

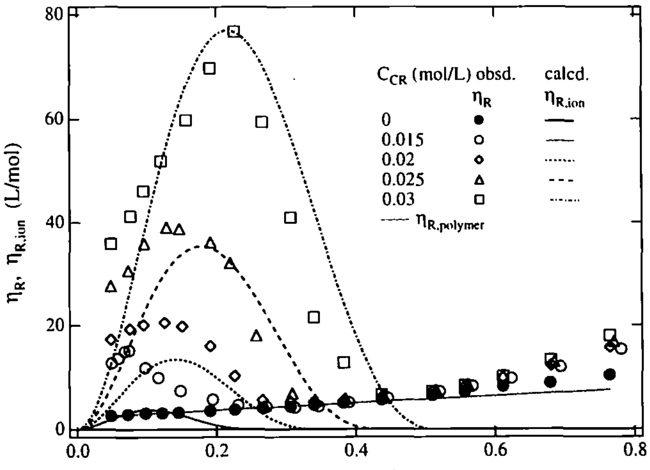

Figure 4 Theoretical calculations of the contribution of the electrostatic interaction to the reduced viscosity, $\eta_{R,ion}$, for $C_{CR} = 0.015$, 0.020, 0.025, and 0.030 mol l^{-1}, as a function of C_{PVA}. The theoretical curves were scaled in order to adjust the maximum of the observed η_R for $C_{CR} = 0.030\ \text{mol l}^{-1}$

by increasing C_{CR}. Since the RK theory does not take account of the viscosity increase due to the presence of polymer chains, the net reduced viscosity, η_R, for a weakly charged polymer solution should be given by the following:

$$\eta_R = \eta_{R,\text{polymer}} + \eta_{R,\text{ion}} \tag{17}$$

where $\eta_{R,\text{polymer}}$ is the reduced viscosity for a non-charged polymer solution. In addition, $\eta_{R,\text{polymer}}$ is a function of the polymer concentration, C, according to the following well known relationship:

$$\eta_{R,\text{polymer}} = [\eta] + k'[\eta]^2 C \tag{18}$$

where k' is the Huggins constant[29]. The value of k' is known to be an invariant with respect to the temperature and the nature of the solvent. The values of $[\eta]$ and k' for a solution of PVA ($DP = 1800$) at 60°C were estimated to be $2.301\,\text{mol}^{-1}$ and 1.30, respectively, for $C_{PVA} \leqslant 0.38\,\text{mol}\,\text{l}^{-1}$. These values are comparable to those obtained by Tager *et al.* ($[\eta] = 3.61\,\text{mol}^{-1}$ and $k' = 1.32$ for an aqueous solution of PVA ($DP \approx 1050$) at 50°C)[30]. It is obvious that the deviation of the observed η_R from $\eta_{R,\text{ion}}$ results from the presence of $\eta_{R,\text{polymer}}$.

Figure 4 clearly indicates that the viscosities of the polymer solutions are drastically changed by the introduction of attached ions to the polymer. This C_{CR} dependence of the maximum in $\eta_{R,\text{ion}}$ is opposite to the general trend observed for polyelectrolytes[24]. We should remind ourselves here that the attached charge density for the PVA–CR complexes is a function of C_{CR} and $C(=C_{PVA})$, which is given by equations (13)–(16b), because it is determined by the complexation equilibrium. On the other hand, the degree of ionization for typical polyelectrolytes is invariant as far as a full ionization is attained. This essential difference results in the opposite dependence of the position and the height of $\eta_{R,\max}$ on the charge density concentration, i.e. C_{CR} in the case of PVA–CR. At higher PVA concentrations, $\eta_{R,\text{ion}}$ becomes zero, recovering the same value of η_R as that of non-charged PVA solutions, i.e. $\eta_{R,\text{polymer}}$.

Time evolution of the reduced viscosity

As indicated above, η_R increases only over the limited region where a maximum appears in the η_R *versus* C_{PVA} plots. *Figure 5* shows plots of the time evolution of η_R. The solid curves are the ones fitted by using an exponential-type function, which is given by the following:

$$\eta_R(t) = (\eta_R^\infty - \eta_R^0)[1 - \exp(-t/\tau)] + \eta_R^0 \tag{19}$$

where η_R^0 and η_R^∞ are the reduced viscosities at time $t = 0$ and $t = \infty$, respectively, and τ is the viscosity thickening half-time. Equation (19) indicates that additional cross-links are formed by ageing at a constant rate of $1/\tau$, as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{\eta_R(t) - \eta_R^0}{\eta_R^\infty - \eta_R^0}\right] = \frac{1}{\tau} \tag{20}$$

The observed data points can be reproduced by using equation (19) except for the low-t region where a different viscosity thickening mechanism may be present.

Figure 6 shows the variation of η_R^0, η_R^∞, and τ with C_{CR}. The dashed line indicates the value of η_R for a non-charged PVA solution having the same C_{PVA}. Since τ is more or less constant ($\sim 27\,\text{h}$), irrespective of C_{CR}, the viscosity thickening mechanism does not change in the concentration region where $C_{CR} \geqslant 0.015\,\text{mol}\,\text{l}^{-1}$. However, η_R^0 and η_R^∞ both increase linearly with C_{CR} in the same C_{CR} region. This experimental evidence indicates that there exists a lower limit of C_{CR} where time-dependent viscosity thickening takes place. Viscosity thickening with time is usually explained by the occurrence of a successive hydrogen bonding process, for example in the case of the PVA–vanadate ion complexes[14]. However, in the case of the PVA–CR ion complexes, a viscosity thickening was observed at 60°C, where hydrogen bonds are believed to be absent. In addition, the good agreement between the observed and calculated viscosity behaviour shown in *Figure 4* suggests that the unique behaviour of η_R for the PVA–CR system can be interpreted without introducing the idea of hydrogen bonds. As has been discussed in ref. 15, the CR molecules themselves have a capability for undergoing viscosity thickening via (1) hydrogen bonding, (2) association of azo and amino groups, and/or (3) stacking of naphthalene groups. At a relatively high temperature, such as 60°C, the association and/or stacking seem to be more favourable, resulting in a slow viscosity thickening. This interpretation does not contradict the assumption made in the theoretical calculation.

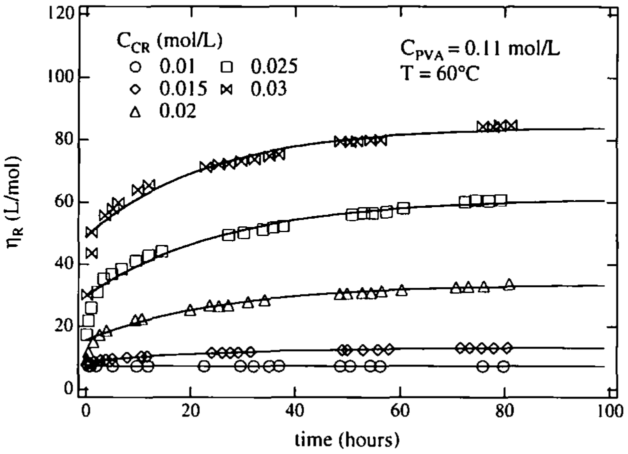

Figure 5 Time evolution of η_R for PVA–CR ion complex solutions with different values of C_{CR}; the continuous curves are fitted using equation (19)

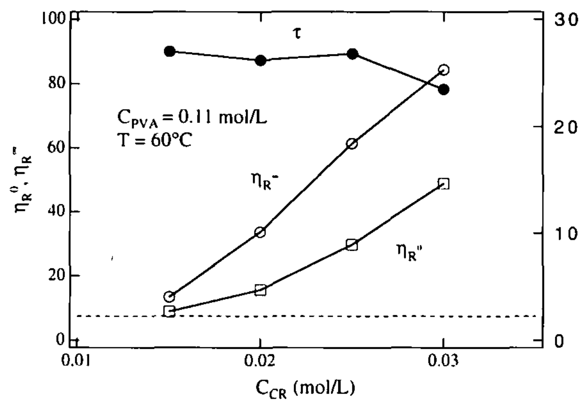

Figure 6 C_{CR} dependence of η_R^0, η_R^∞, and τ; the dashed line indicates η_R for a non-charged PVA solution

CONCLUSIONS

The viscosities of PVA–CR ion complexes in aqueous solutions were measured as functions of the PVA (C_{PVA}) and CR (C_{CR}) concentrations. A comparison of the crosslinker concentration dependence of the reduced viscosity, η_R, between the PVA–CR and PVA–borate complexes indicated the presence of strong electrostatic repulsive interactions in the PVA–CR complexes.

The C_{PVA} dependence of η_R showed some interesting features, namely (1) the appearance of a maximum at a given PVA concentration (C_{PVA}) and (2) a time evolution of η_R, but only in the regime where the maximum appears. For low values of C_{CR}, the behaviour of the reduced viscosity, η_R, is very similar to that observed for polyelectrolyte solutions without salt. However, for the high C_{CR} regime, the C_{PVA} dependence of η_R has a distinct maximum, with this maximum becoming higher with increasing C_{CR}. Although this tendency is similar to that observed for polyelectrolytes, the fact that the maximum moves in the direction of higher C_{PVA} values with increasing C_{CR} is opposite to the typical polyelectrolyte behaviour. These experimental findings were interpreted by using theoretical calculations of the electrostatic effect on the viscosity. The viscosity thickening could be fitted with an exponential-type function, which had a half-time τ of ~27 h, irrespective of C_{CR}.

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