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Rheological Study of Poly(ethylene oxide) in Aqueous Salt Solutions at High Temperature and Pressure

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ABSTRACT: The effects of pressure and temperature on the rheological properties of poly(ethylene oxide) (PEO) aqueous solutions, with and without added inorganic salts, are reported. A slight decrease of the viscosity at low temperatures and an increase of the viscosity at high temperatures with increasing pressure were noted. However, the most striking effect was the lowering of the phase separation temperature with increasing pressure, which manifested itself in large changes in the viscosity of the solutions. This effect is proposed to be due to the lowering of the solvent quality of the water for PEO, brought about by the disruption of the hydrogen bonding in the water which occurs on increasing the pressure.

Introduction

The rheological properties of polymer solutions are, in large part, controlled by the polymer−solvent interactions.[1−3] Cook *et al.*[4] have reported that the viscosity of aqueous poly(ethylene oxide) (PEO) solutions at 20 °C decreases with increasing pressure and that the phase separation temperature decreases sharply when the pressure exceeds 3500 bar. The explanation provided by the authors is that the hydrogen bonding, between the water and the PEO molecules is disrupted at high pressure, and, as a consequence, there is a reduction in the solvent quality. The change of the viscosity of pure water with increasing pressure follows this behavior below 35 °C in the pressure range of 0−200 MPa. However, above this temperature, the viscosity increases with increasing pressure.[5] The decrease of the viscosity with increasing pressure is caused by the reduction in the hydrogen bond between water molecules, which brings about a change in the cluster structure of the water. Recently, very revealing work, regarding the induced changes in the water structure[6,7] based on the neutron diffraction, showed that the characteristic tetrahedral structure of water is disrupted by changes in pressure and temperature and also by the dissolution of ions in water. The effects produced by these variables—temperature, pressure, and the ions—are to some extent equivalent. Moreover, it was noted that the effectiveness of various salts at disrupting the water structure was qualitatively consistent with the Hofmeister series, which describes the efficacy of the salts in precipitating proteins from water.[8]

PEO molecules in water exhibit strong hydrogen bonding and hydrophobic interactions and show many properties similar to those of proteins in water. For example, PEO exhibits a salting-out behavior, and the order of the effectiveness of the ions is similar to that of the Hofmeister series for proteins.[9] In this paper, we examine the effects of changes in the pressure and the temperature on the viscosity and phase behavior of aqueous PEO solutions in the presence of various salts.

Experimental Section

Materials. PEO with an approximate weight-average molecular weight of 10^6, as received from the Aldrich Chemical Co., UK, was used to prepare 2% (w/w) aqueous solutions using deionized water. The ionic strength of these solutions was changed by the addition of the various electrolytes into the deionized water. Analytical grade potassium chloride, potassium sulfate, and sodium carbonate were obtained from the Aldrich and used without further purification.

Method. The rheological properties were measured by a modified Haake Searle-type viscometer, which was incorporated into a high-temperature and -pressure chamber. The maximum operating pressure and temperature were 1000 bar and 170 °C, respectively, and the maximum measurable shear stress was 55 Pa. In the present work, the asymptotic dynamic shear stress was measured at a constant shear rate of 226 s^{-1}. Further details concerning this high-pressure and -temperature viscometer are to be published elsewhere.[10]

The effect of temperature was determined by measuring the stress at the designed temperature and then incrementally increasing the temperature. The effect of pressure, at a particular temperature, was determined by measuring the stress at different pressures. During these measurements, the shear induced by the viscometer was maintained while the pressure was changed, and the data were continuously collected. When the pressure achieved the required values, the shear stress at that pressure was determined. This reduced the errors and fluctuations in the transducer response. An example of the data is shown in Figure 1. The measured shear stress was observed to be invariant with time at a given temperature and pressure in this study. In all the work reported here, the viscosity quoted is an apparent viscosity, i.e., the apparent viscosity at a nominal shear rate of 226 s^{-1}. Some data at atmospheric pressure were also obtained with a Bohlin VOR rheometer.

Results

Figure 2 shows the pressure-dependent relative viscosity η^* ($\eta^* = [\eta_p - \eta_1]/\eta_1$, where η_p and η_1 are the viscosities at 1 and p bar, respectively) at different temperatures for 2% PEO in an aqueous solution with no added electrolytes. The relative viscosity of the solution decreases slightly with increasing pressure at temperatures below 35 °C, which is similar to the result reported by Cook *et al.*[4] However, at temperatures above 35 °C, the viscosity increases with increasing pressure, and the higher the temperature, the more pronounced is this effect. The effects of temperature and pressure on the viscosity for this PEO solution are

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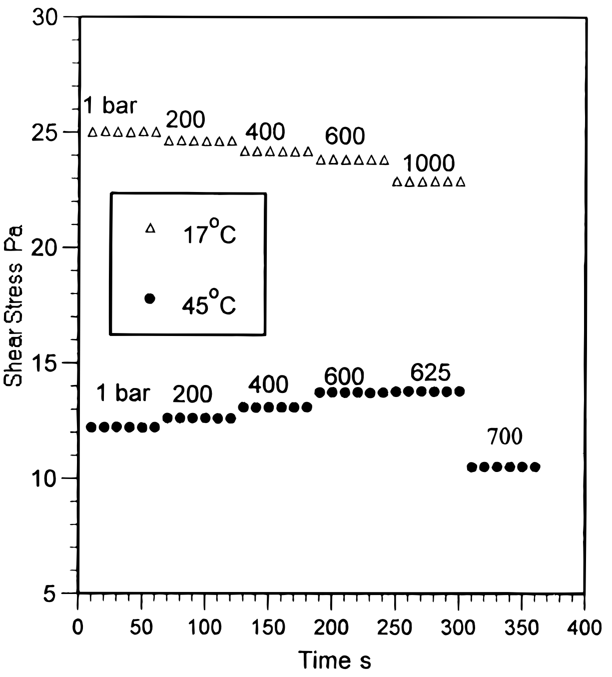

Figure 1. Shear stress at a shear rate of 226 s^{-1} for 2% PEO in 0.3 M Na_2CO_3 aqueous solution at different temperatures and pressures. The numbers above the curves represent the pressure at which the measurement data are collected.

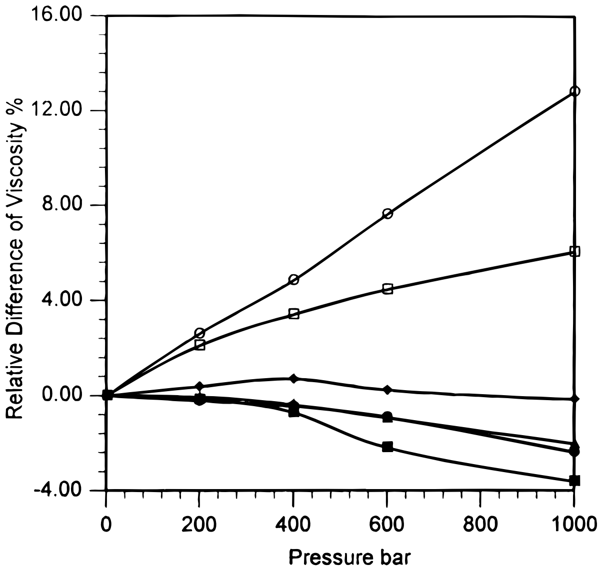

Figure 2. Plot of pressure-dependent relative viscosity η^* for 2% PEO in aqueous solution at different temperatures: ■, 17; ●, 20; ▲, 25; ◆, 35; □, 60; and ○, 80 °C.

also similar to the effects observed for pure water.[5] It should be mentioned that, even at the phase separation temperature (about 100 °C at 1 bar for PEO in pure water), the viscosity still increases with increasing pressure.

To demonstrate the influence of the ionic strength, an experiment similar to that discussed above was carried out for 2% PEO in 0.3 M Na_2CO_3 aqueous solution, and the results are shown in Figure 3. The shear stress of the solution decreases with increasing pressure below 30 °C and then increases when the temperature is above 30 °C. However, more significant changes occur when the temperature is greater than 40 °C. Initially, the shear stress increases with increasing pressure, and then it dramatically decreases with further increasing of the pressure. It is interesting to note that the shear stress recovers to its original value quickly when the pressure is released; the time constant is less than 150 s. The higher the temperature, the lower are the pressures required to induce such sharp decreases of the shear stress. This decrease in the shear stress with increasing pressure corresponds to a collapse of the polymer chain morphology resulting from the induced phase separation.[2] The phase boundary so defined corresponds to the lower critical solution temperature.

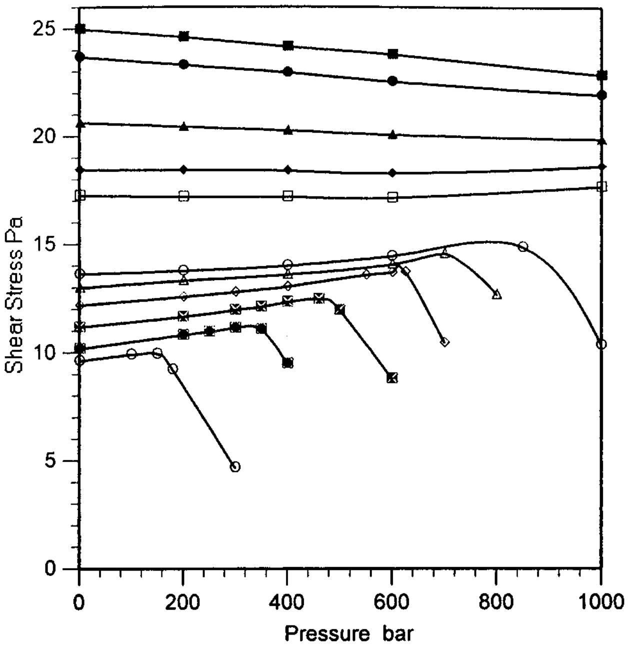

Figure 3. Shear stress at a shear rate of 226^{-1} and pressure relationship for 2% PEO in 0.3 M Na_2CO_3 aqueous solution at different temperatures: (top to bottom) ■, 17; ●, 20; ▲, 25; ◆, 30; □, 33; ○, 40; △, 43; ◇, 45; ×, 48; ⊡, 50; and ⊙, 54 °C.

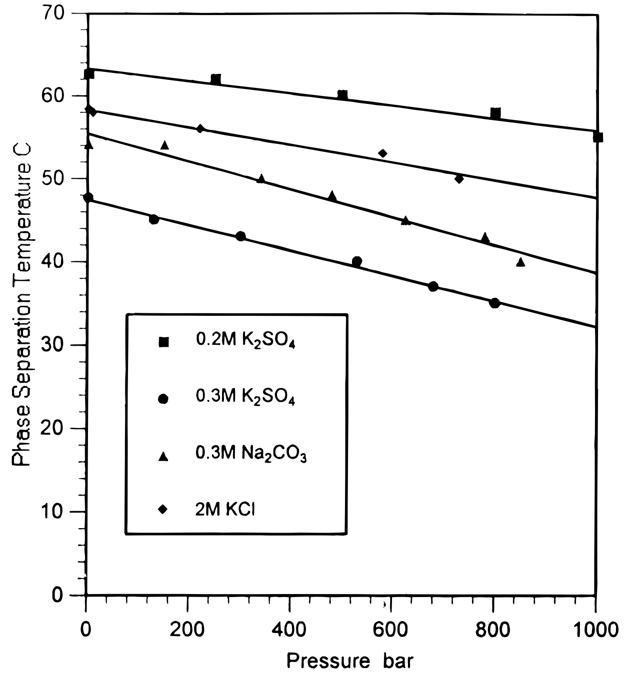

Figure 4. Phase separation temperatures for 2% PEO in different salt solutions at different pressures. The data at 1 bar are measured by Bohlin VOR viscometer.

Figure 4 shows the interrelationship between the phase separation temperature and the applied pressure for 2% PEO in aqueous solution with different salts and salt concentrations. It may be seen from this figure that the phase separation temperatures decrease in an approximately linear manner with increasing pressure for all of the four solutions shown. The data indicate that, for higher salt concentrations, the lower is the phase separation temperature at that pressure. The effects for different salts show that their effectiveness is similar to that predicted from the Hofmeister series and also to that observed for PEO solutions at atmospheric pressure.[9]

Discussion

PEO aqueous solutions show an inverse solubility–temperature relationship and exhibit a lower critical solution temperature (LCST) at about 100 °C at 1 bar.[9] In water, a network structure has been shown to form between water molecules and polymer chains, corresponding to two or three water molecules associating with each -CH_2CHO- segment, through hydrogen bonding, and it has also been shown that these interactions produce an ordered water structure adjacent to the polymer chain.[11] At relatively low temperatures, the viscosity of these polymer solutions decreases with increasing pressure. This is a result of the disruption of the hydrogen bonding mainly between the water molecules and polymer chains and also between the water molecules, consequently inducing a diminution of the solvent quality and the gyration radius of the PEO chains.[12] At higher temperatures, because of the thermally induced disruption of the hydrogen bonding, the effect of pressure on hydrogen bonding is less significant. On the other hand, the free volume effect becomes more pronounced, and hence the viscosity increases when the pressure increases; as the density of the solution increases due to the application of pressure, less free volume is available to facilitate molecular motion of the polymer chains. In the present experimental pressure range of up to 1000 bar, no influence of the pressure upon the phase separation temperature for PEO aqueous solution was observed. This is consistent with Cook's work, in the same pressure range, for similar polymer solutions.[4] However, when ionic salts are added to the polymer solutions, the hydrogen bonding in the solutions is disrupted by the ions. This effect has been observed as a reduction of the viscosity of ion-doped polymer solutions compared with that of undoped polymer solutions. When the pressure increases at relatively low temperatures, the observed decrease in the viscosity with increasing pressure indicates that the hydrogen bonding is not completely suppressed by the salts over the current concentration range. Sawamura *et al.*[5] have concluded, from studies of the viscosity of aqueous sodium chloride solution at high pressure and high temperature, that the hydrogen bonding in water is not entirely destroyed until the salt concentration is above 4 M. When the pressure is increased at higher temperatures, the viscosity increases with increasing pressure because of the effect of temperature on the hydrogen bonding structure and the reduction in the free volume induced by the pressure. It is notable that the temperature at which the pressure dependence of the viscosity changes sign, from negative to positive, is different for different salts in solutions and that it decrease with increasing salt concentration. These transition temperatures are consistent with the ions' effectiveness in suppressing hydrogen bonding and show that the effects of the salts and the temperature are comparable in their actions. These data are collected in Table 1.

Table 1. Transition Temperature and Phase Separation Temperature for PEO Aqueous Solutions at Atmospheric Pressure

	water	0.2 M K_2SO_4	2 M KCl	0.3 M Na_2CO_3	0.3 M K_2SO_4
transition temp,[a] °C	35–40	30–35	30–35	25–30	20–25
phase separation temp,[b] °C	100	62	58	54	49

[a] The temperature at which the viscosity of the solution is relatively independent of the pressure. [b] The temperature for phase separation at 1 bar.

With further increases of the temperature (near the phase separation temperature of the polymer solutions at ambient pressure), a marked decrease in the measured shear stress with increasing pressure was observed. The sharp decrease of the shear stress is due to the phase separation of the polymer solutions induced by the pressure. The increase of the pressure decreases the phase separation temperature of PEO in ion-doped solutions (see Figure 4), but no comparable effect has been observed for the same solutions without salts in current pressure range up to 1000 bar. The cloud point measurements, described by Cook *et al.*[4] showed that the phase separation temperature for PEO in aqueous solution was not affected significantly by pressure until 3000 bar. Thus, the addition of the salts enhances the effect of the pressure on the phase separation temperature for PEO. It is well known that the phase separation temperatures of PEO solutions decrease after the addition of the salts at ambient pressure.[9] The phase separation temperatures of PEO in aqueous salt solution, measured by using a conventional Bohlin VOR viscometer at ambient pressure 1 bar, are shown in Table 1. It shows that the phase separation temperatures are consistent with the transition temperatures, and both of them are determined by the solvent quality.

Conclusions

The reduction of the solvent quality for aqueous PEO solutions, which is induced by the disruption of the intermolecular bonding mainly between the water molecules and the polymer chains, can be achieved in three ways. Increasing the temperature imparts more thermal energy into the system, which naturally causes a reduction in bond strength. Adding electrolytes which disrupt the hydrogen bonding by becoming hydrated produces a similar effect. We note that the Hofmeister series for electrolytes, originally developed for rationalizing protein salting-out from aqueous solutions, is followed for the deterioration of the solvency in PEO solution. The application of pressure also disrupts the hydrogen bonding by forcing the molecules closer together.[8] These effects, which are different in their cause, all affect the nature of the hydrogen bonding existing in the solutions in a comparable way and are similar in their consequences, i.e., increasing temperature, electrolyte concentration, or pressure can cause phase separation of PEO in aqueous solutions. These results have potential importance in understanding the interactions between PEO and water and in any process where aqueous PEO solutions are handled at high pressure, whether it be in aqueous drilling fluids or in extrusion engines to name just two examples.

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