Colloid & Polymer Science Colloid Polym Sci 272: 516–522 (1994)

Role of ionic species and valency on the viscoelastic properties of partially hydrolyzed polyacrylamide solutions

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Abstract: The effects of ionic species and valency on the viscoelastic properties of partially hydrolyzed polyacrylamide solutions were examined. Two viscoelastic parameters were considered, i.e., average relaxation time, λ_M^0 and steady state compliance, Je^0. Both these parameters are independent of ionic species of monovalent salts. However, λ_M^0 decreases with increasing salt concentrations. Divalent salts reduce the values of λ_M^0 by as much as 10 times. On the other hand, Je^0 is independent of salt concentrations and valency. The effects of monovalent salt on three different polyacrylamide samples of varying degree of hydrolysis and MW were also examined.

Key words: Polyacrylamide – ionic – valency – viscoelasticity – salt effect

Introduction

In our previous paper [1], we reported on the effect of ionic species and valency on the steady shear behavior of partially hydrolyzed polyacrylamide solutions. It was shown for polyelectrolytes that the nature of the solvents drastically alter the rheological behavior of polymer solutions. In many applications where salts of different species and valency are encountered (such as water treatment, drag reduction, enhanced oil recovery, etc.), appreciable understanding of these effects is essential to the optimum performance of the polymers used. Such effects on the dynamic properties of dilute polymer solutions have not been extensively studied.

However, some studies have been carried out for concentrated systems such as poly(methacrylic acid) [2] and poly(sodium acrylate) [3] at the resonant frequency where gelation occurs. Sakai et al. [4] investigated the viscosity, the first normal-stress difference, and the compliance function of 1 to 4 wt% of poly(sodium acrylate) at various NaCl concentrations. In order to obtain solutions with a measurable viscosity range, they used 30% aqueous glycerine as the solvent. A more comprehensive study was reported by Okamoto et al. [5, 6] on 0.15 wt% of poly(acrylic acid) and poly(methacrylic acid) at frequencies from 2 to 500 kHz. The measurements were made at different degrees of polymerization and different concentrations of NaCl. Rosser et al. [7] examined the dynamic properties of dilute solutions of sodium poly(styrene sulfonate) in the presence of glycerol and sodium chloride salt. The frequency dependence of storage and loss moduli were modeled using a hybrid relaxation spectra that combines the rodlike and coil-like behavior. Recently, the viscoelastic properties of poly(M-methyl-2-vinyl pyridinium chloride)s were studied by Yamaguchi et al. [8]. They examined the steady-state compliance of the polyelectrolyte in the presence of added salt.

It is evident that studies of viscoelastic behavior of polyelectrolytes in different solvent environments are scarce. One reason is that dynamic properties of dilute polyelectrolyte solutions are difficult to measure. Most rheological equipment is designed for applications such as concentrated polymer solutions or melts. However, with the introduction of sensitive rheometers such as the Contraves Low Shear 30-Sinus, measurement of viscoelastic properties of polymer solutions is now possible.

In this study, the dynamic properties of 500 and 1000 ppm polyacrylamide solutions in different salt environments are investigated. The solutions are dilute as the measured zero shear viscosity is linearly dependent on the polymer concentration [9]. The effects of ionic species and valency on the dynamic properties are reported.

Experimental method

Preparation procedure for the test solutions is adequately described in our previous publication [1]. The dynamic properties were measured at 20 °C using a Contraves Low Shear-30 rheometer equipped with a concentric cylinder system. The instrument is capable of measuring moduli at frequencies ranging from 10^{-3} to 10 rad/s. This rheometer is extremely sensitive and can measure moduli down to about 10^{-4} Pa at frequency of 10^{-3} rad/s [10]. It makes use of a light compensation system to measure any movement arising from the torque response of the fluids.

Results and discussion

1. Storage and loss moduli

The effects of salt concentration on the storage and loss modulus of 500 ppm Separan AP30 solutions with different NaCl concentrations are shown on Figs. 1 and 2. For the purpose of clarity, only selected data for several salt concentrations covering the lower and upper limits are shown to illustrate the trend of the change of dynamic properties in the presence of different amount of salts. At a particular frequency, addition of salt drastically reduces values of G' and G''. For example, addition of 4×10^{-3} M NaCl reduces the magnitude of G' by more than an order of magnitude at low frequency. The effect is less at higher frequency. Such a reduction is consistent with the observation in the steady shear properties [1]. It is also evident that at the low frequency region, the slopes of G' and G'' are 2 and 1, respectively. In this region, certain viscoelastic properties such as relaxation time and compliance are independent of frequency. These two parameters will be examined later.

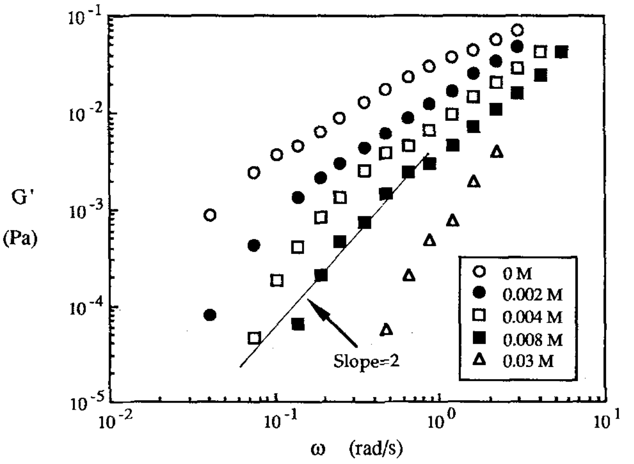

Fig. 1. Storage modulus of 500 ppm Separan AP30 in different NaCl concentrations

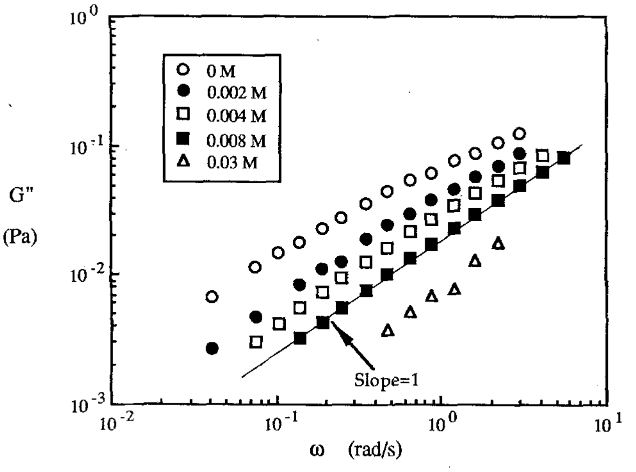

Fig. 2. Loss modulus of 500 ppm Separan AP30 in different NaCl concentrations

Comparisons of the effects of monovalent (NaCl) and divalent ($BaCl_2$) salts on the storage and loss moduli of the 500 ppm Separan AP30 solution are shown in Figs. 3 and 4. The effects of salt on dynamic properties are similar to those on steady shear data. At low frequency ($\omega = 0.252$ rad/s) the differences in the values of G' and G'' between the monovalent and divalent salt are about 10 and 5 times, respectively. These differences diminish with increasing frequency.

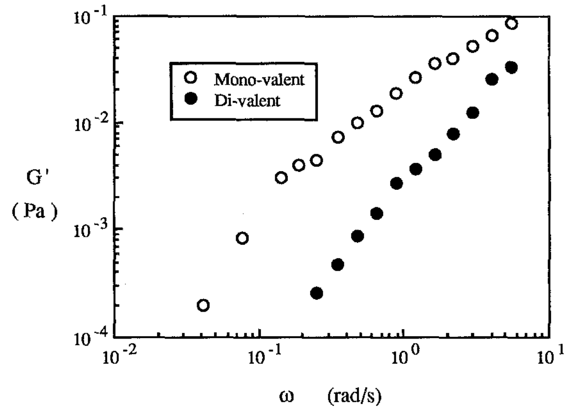

Fig. 3. Comparison of storage modulus of 500 ppm Separan AP30 in 0.001 M monovalent and divalent salt

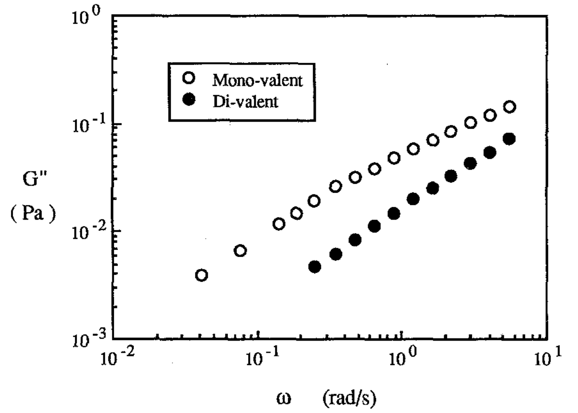

Fig. 4. Comparison of loss modulus of 500 ppm Separan AP30 in 0.001 M monovalent and divalent salt

2. *Relaxation time and compliance*

At the low frequency region, the limiting condition is approached whereby the elastic parameters are independent of frequency. Two important elastic parameters approaching zero deformation rate are evaluated, namely,

a) Average relaxation time, λ_M^0;
b) Steady-state compliance, Je^0.

The relationships between the above parameters and the valence and ionic species were examined.

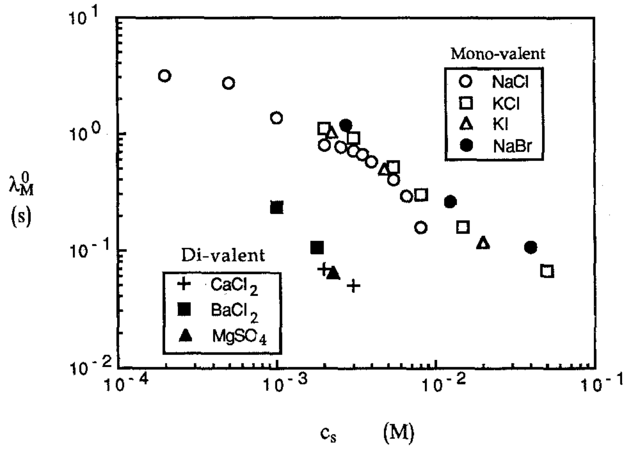

Fig. 5. Effect of ionic species on average relaxation time of 500 ppm Separan AP30

a) Average relaxation time, λ_M^0

The average relaxation time can be evaluated from the oscillatory data in the limit of zero deformation rate:

$$\lambda_M^0 = \lim_{\omega \to 0} \frac{G'}{\omega^2 \eta_0}, \qquad (1)$$

where η_0 is the zero shear viscosity.

i) Effect of ionic species

The average relaxation times of 500 and 1000 ppm polyacrylamide in 2×10^{-4} to 1×10^{-1} M NaCl, KCl, KI, and NaBr salts were determined from Eq. (1). The results were plotted in Figs. 5 and 6. Two main features can be drawn from the figures:

a) The relaxation time of polyacrylamide solutions is independent of ionic species of the same valency. This is consistent with the steady shear data as represented by the zero shear viscosity [1]. The present results confirm that the size and types of ionic species do not play a major role in altering the steady and dynamic properties of dilute aqueous polymer solutions. The only parameter that is important is the ionic strength of solvent.
b) λ_M^0 decreases with increasing salt concentrations. At $c_S > 10^{-3}$ M, the values of λ_M^0 decreases linearly with salt concentration

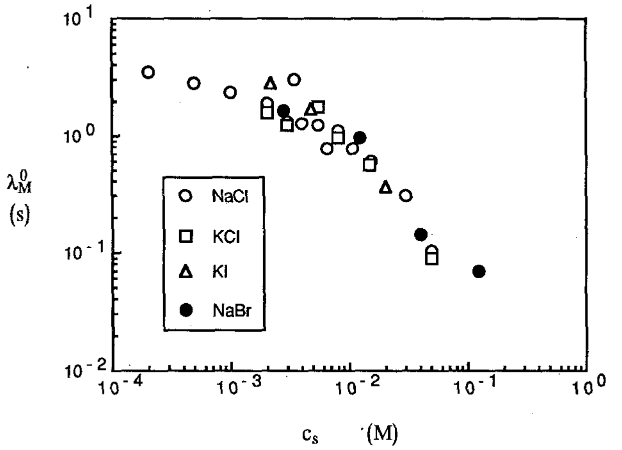

Fig. 6. Effect of ionic species on Maxwell relaxation time of 1000 ppm Separan AP30

(in the double logarithmic representation). For example, λ_M^0 decreases from 1 to 0.1 s when the salt concentration increases from 10^{-3} to 10^{-2} M for the 500 ppm Separan solution.

Physically, λ_M^0 represents the time polymer coils take to relax and return to its stable state. Hence, the larger the value of λ_M^0, the more elastic the fluid. At low salt concentration (say, $c_S < 10^{-3}$ M) the polymer coils are in their extended conformation. The size of the coils as defined by the radius gyration is much larger than at theta-condition. However, as more salts are added, the repulsion between the charged groups are screened, resulting in a sharp decrease in the size of the polymer coils. The polymer coils are somewhat altered to one that is more compact and rigid in nature and this renders the fluid to be less elastic. Addition of salt is analogous to altering the solvent quality – from a good to a poor solvent at high salt concentrations. It was shown previously [11] that addition of salt alters the molecular expansion factor α significantly. The values of α change from 4.5 at c_S of 10^{-3} M to 1.4 at c_S of 5×10^{-1} M. At theta-condition, α equals unity.

The large change in the elasticity at $c_S > 10^{-3}$ M suggests that hydrolyzed polyacrylamide is fairly sensitive to salt environment. Such behavior will result in a reduction in its effectiveness in applications such as drag reduction and enhanced oil recovery where high salt contents are encountered. In such applications, the desired viscosity and elasticity will not be achieved.

ii) Effect of ionic valency

In contrast to the steady shear properties, only a very limited amount of dynamic data was obtained for di-valent salts. The Contraves Low-Shear 30-Sinus is not capable of accurately measuring the dynamic properties of solutions with η less than 4×10^{-3} Pa.s. Moreover, at such low viscosity, the inertia effects become significant in the high frequency region.

Qualitative comparisons of the effects of mono and divalent salts are shown in Fig. 5. The divalent salts used are $CaCl_2$, $BaCl_2$, and $MgSO_4$. It is apparent from the results that addition of a divalent salt decreases the magnitude of λ_M^0 by approximately one order of magnitude respectively as compared to monovalent salt. The strong effect of divalent salts on the dynamic properties is consistent with the observation for steady shear flow.

The results in Fig. 5 suggest that hydrolyzed polyacrylamide may not be a very effective additive in enhanced oil recovery and drag reduction applications where high valency ionic species are normally present in the system. The effectiveness of such polymer additives is reduced even further in the presence of Fe^{3+} ions commonly found in metal pipes.

b) Steady state compliance, Je^0

Another useful parameter for characterizing the elastic behavior of polymer solutions is the steady state compliance, Je^0. In molecular terms, it measures the average distortion of the polymer coils during flow when ample time has been allowed for the molecular distribution function to become independent of time [12]. Mathematically it is defined as:

$$Je^0 = \lim_{\omega \to 0} \frac{G'}{\omega^2 \eta_0^2} \tag{2}$$

Je^0 is related to the average relaxation time as shown below:

$$Je^0 = \frac{\lambda_M^0}{\eta_0} \tag{3}$$

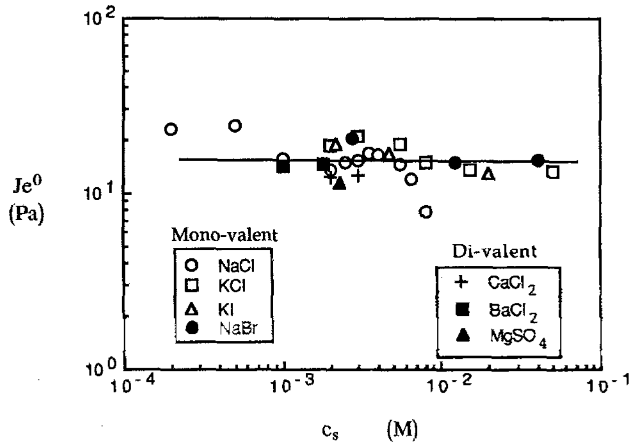

Fig. 7. Effect of ionic species on steady state compliance of 500 ppm Separan AP30

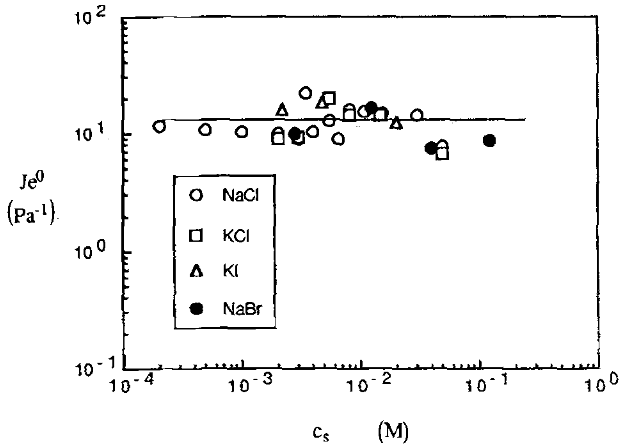

Fig. 8. Effect of ionic species on steady state compliance of 1000 ppm Separan AP30

Hence, the magnitude of Je^0 gives a measure of the energy stored and recovered per cycle [13].

Various methods have been used to measure Je^0, such as creep recovery [14, 15], stress relaxation [16], first normal stress difference [17, 18], and storage modulus [19, 20]. Depending on the methods used, the values of Je^0 can vary by approximately a factor of two when compared with the results obtained from creep recovery studies [21].

i) *Effect of ionic species*

The steady state compliances of 500 and 1000 ppm polyacrylamides in NaCl, KCl, KI, and NaBr salt solutions were determined from Eq. (3). The results were plotted in Figs. 7 and 8 for 500 and 1000 ppm, respectively.

It is evident from the figures that the steady state compliance does not depend on the ionic species nor the salt concentration for a given valency salt. All the data for different salts appear to scatter around a horizontal line indicating that Je^0 is independent of salt concentrations. This means that the energy stored and recovered in a given polymer coil is independent of the coil conformation. For both the 500 and 1000 ppm solutions, the magnitude of Je^0 is about 15 for salt concentrations ranging from 2×10^{-4} to 1×10^{-1} M.

The present findings appear to contradict with the results of Yamaguchi et al. [8] in which Je^0 was found to be proportional to the salt concentration in the dilute solution regime. On the other hand, Kusamizu et al. [22] and Sakai et al. [17] concluded from their results that Je^0 does not depend on the choice of solvent so long as good solvents are used. The present results seem to concur with their findings.

ii) *Effect of ionic valency*

Figure 7 depicts the effect of monovalent and divalent salts on the steady state compliance. Despite the limited data points for divalent salts, Je^0 appears to be independent of the valency of salts present in solution. It is seen from Fig. 5 that a 10-fold decrease in λ_M^0 is obtained when divalent salts are used. A similar decrease in the zero shear viscosity η_0 has also been observed [1] when a divalent salt is used instead of a monovalent salt. Since both λ_M^0 and η_0 decrease by about the same order of magnitude when divalent salts are added, Je^0 is expected to remain constant, independent of the ionic valency and salt concentration.

3. Effects of monovalent salt on the viscoelastic properties of polyacrylamides of different molecular weight

Commercial polyacrylamides come in different grades, each with a particular ionic content and average molecular weight. The dynamic

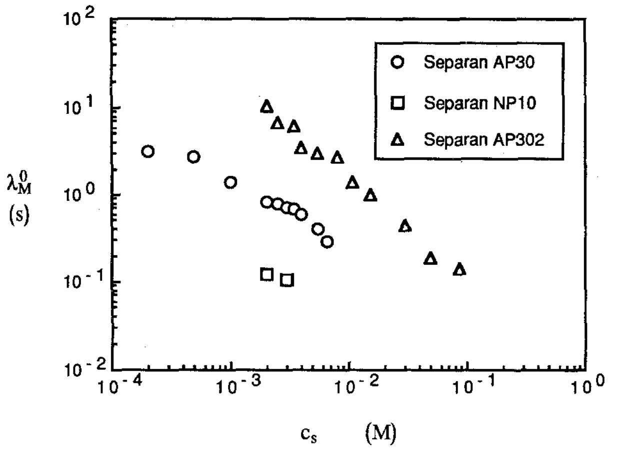

Fig. 9. Effect of monovalent salt on Maxwell relaxation time of 500 ppm polyacrylamide polymers

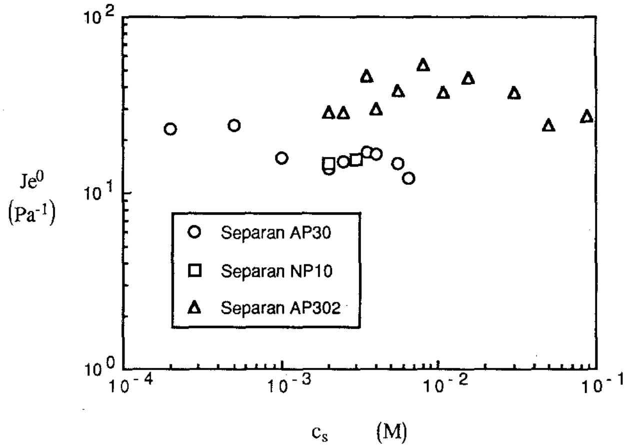

Fig. 10. Effect of monovalent salt on steady state compliance of 500 ppm polyacrylamide polymers

properties of 500 ppm Separan NP10, AP30, and AP302 solutions as expressed by λ_M^0 and Je^0 are measured and their relative behavior in various concentrations of NaCl are shown in Figs. 9 and 10. The average relaxation time, λ_M^0 decreases significantly with increasing salt concentration. As would be expected, Separan AP302 (being the polymer with the highest molecular weight) exhibits a large elasticity, particularly at the low salt region compared with Separan AP30 and NP10. For example, at c_S of 10^{-3} M, the average relaxation time of Separan AP302 is about 10 s compared with 1 s and 0.1 s for Separan AP30 and NP10, respectively. The steady state compliance, Je^0 for each polymer is depicted in Fig. 10. It can be observed that Je^0 for Separan AP302 is marginally higher than AP30 or NP10 which seems to be consistent with the Rouse theory (i.e., $Je^0 \propto M$) for a fixed polymer concentration. However, the degree of hydrolysis may also affect the value of Je^0. For example, Separan NP10 is relatively neutral compared to AP30 and AP302. Inspite of its lower molecular weight compared to the other two polymer species (2×10^6 cf 4×10^6 and 8×10^6, respectively), its Je^0 value is the same as that of AP30.

Conclusions

The viscoelastic properties of dilute polyacrylamide solutions are strong functions of valency and salt concentrations. The elasticity as measured by the average relaxation time decreases by a factor of 10 when a divalent salt is used instead of monovalent salt. However, the steady state compliance does not depend on either salt concentration or valency.

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Received July 7, 1992;
accepted September 23, 1993

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