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Additive effect on the behavior of water-soluble hydrolyzed polyacrylamide copolymer

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Abstract

A physico-chemical study of the hydrolyzed polyacrylamide (AD37) solution, using rheology and viscosity methods was reported. The viscosity of polyelectrolytes is measured in the presence effect of different additive (NaCl salt, N-dodecylpyridinium chloride surfactant (DPC) and poly(4-vinylpyridine). It was found that the DPC causes a larger reduction of the viscosity of AD37 solution than does NaCl. This difference is due to the presence of the second type of interaction with DPC (hydrophobic interaction). The DPC chains can bind to the polyion chain cooperatively in the form of the so-called (polymer-induced) micelles. The result shows also that the effects are greater in the presence of the P4VP. The contact between the polyelectrolyte (AD37) and the DPC surfactant or P4VP chains under the conditions used enables a variety of types of interaction, depending on the relative concentrations.

Keywords: Viscosity, Rheology, AD37, P4VP, DPC, Interactions.

1. Introduction

Polyelectrolyte solutions have been studied extensively for both theoretical and experimental purposes. Due to electrostatic interactions between the charged groups along the polyelectrolyte chains, its solutions behaves differently than the neutral polymers for activity coefficients, osmotic coefficients, as well as transport properties like, viscosity, diffusion, etc. [1–4]. In solution phase, progressively hydrolyzed polyacrylamide (PAM) develops varied charge densities on the polymer backbone. Hydrolysis of amide groups in the alkaline condition, adsorption of nonionic [NPAM] [5–8], anionic [9–11] and cationic [12, 13] types of PAM on charged surfaces at different pH media are documented in literature [14, 15]. If hydrolyzed-PAM is dissolved in water [16], it behaves like weak polyelectrolyte with charged COO^- on the backbone. In this charged PAM, relative dissociation of the ionic groups is a function of solvent polarity and the distribution and alignment of the charged dipoles along the chain are expected to play decisive role on the final state of conformation of the polymer chain [14]. Partially hydrolyzed PAM is thus expected to develop fascinating solution behavior especially in aqueous–non-aqueous mixed solvents. Although, some studies on solution viscosity properties of PAM in water are available in the literature, similar studies of hydrolyzed PAM in other solvents or co-solvents are little [17–24].

In the work discussed in this paper, we studied the behaviour of the hydrolyzed polyacrylamide (AD37) solution, using rheology and viscosity methods.

We studied also the effect of the additive (NaCl salt, N-dodecylpyridinium chloride surfactant (DPC) and poly(4-vinylpyridine) (P4VP)) to the AD37 in aqueous solution at 25 °C. We can consider in this work that the NaCl and the DPC charge is positive, similar to that of the P4VP cations. We compared the interactions between AD37 polyelectrolyte and P4VP, DPC and Nacl if there are similar. The new point we would like to elucidate is the hydrophobic character of the DPC alkyl chain and P4VP chains. We present here our results from viscosity measurements, in aqueous solution.

2. Materials and methods

2.1. Apparatus

An Ubbelohde capillary viscometer was used to measure the viscosities of polymer solutions. The viscometer was placed in a thermostated bath at appropriate temperature controlled within the range of ±0.1 °C.

The rheological measurements were performed using a rheometer Brookfield DV-III+ type. This rheometer measure the evolution of the viscosity according to the shear rate.

2.2. Products

Copolymer AD37 based on hydrolyzed acrylamide was provided from Rhône –Poulenc (France). Its rate carboxylate function is $\tau = 0.27$, as determined by^{13}C NMR and potentiometry [25–27]. Its weight-average molar mass was estimated by light scattering to be 5×10^{6} g/mole [25–27].

The surfactant N-dodecylpyridinium chloride (DPC) was provided by Aldrich company. Its molecular mass is 283.5 g/mole.

Poly(4-vinypyridine) (P4VP) is prepared by radical polymerisation of 4-vinylpyridine in methanol, under vacuum, with azo-bis-isobutyronitrile (AIBN) as initiation agent, as described elsewhere [28]. Its molar mass is estimated at 4.10^{4} g. mol^{-1}, by light scattering technique.

3. Results and discussion

3.1. Viscosimetric study of AD37 aqueous solution

The properties of polyelectrolyte solutions in water are extremely sensitive environment. It is well known that the presence of a simple salt reduces the viscosity of the polyelectrolyte considerably [29, 30]. Reduced viscosity (η_{red}) is calculated as follows Eq. (1):

$$\eta_{red} = \frac{\eta - \eta_0}{\eta_0} x \frac{1}{C} \qquad (1)$$

Where C is the polymer concentration; η and η_0 are absolutes viscosities of polymer and solvent respectively.

Figure 1 shows the plots of reduced viscosity of the AD37 according to its concentration in the presence and in absence of salt. Here, a characteristic behavior of the viscosity of polyelectrolyte solutions is observed. In absence of NaCl salt, reduced viscosity decreases greatly with increasing AD37 concentration. Indeed, the reduced viscosity remains constant with a value of 3350 ml.g^{-1} for an interval of concentration ranging between 2.10^{-4} and 5.10^{-4} g.ml^{-1}.

The addition of a simple electrolyte results in shielding of ionic groups on the polyion. Consequently, the coil dimension reduces and leads to a decrease in viscosity. The intrinsic viscosity [η] of the AD37 is determined by extrapolation at the origin of the concentrations of this polymer charged in the presence of NaCl (0.1 N). This value is about 2850 ml.g^{-1}. This result is in agreement with the literature [31]. Thus, we obtain the viscosity average masse of approximately $2.48.10^{6}$ g.mol^{-1} using the equations of Schwartz [25-27] Eq.(2):

$$[\eta] = 5\times10^{-3} M^{0.9} ml/g \qquad (2)$$

3. 2. Rheological study of AD37 solutions

Figure 2 and 3 shows the variation of the viscosity and the shear stress as a function of shear rate for AD37 for different concentration of polymer. For all samples, as the shear rate increased, the typical behavior of pseudoplastic fluid is observed.

The stress increases with the increase of shear rate, while the viscosity decreases continuously. The results in Figure 2 indicate also that the viscosities of the systems increase as AD37 concentration increases. This was probably due to the formation of network structure between AD37 chains caused by inter-chain entanglements at higher concentrations of this polyelectrolyte. When the shear rate increases, a shear thinning behavior is observed, the network structure is deformed. Indeed, the shear stress (τ) and shear rate ($\dot{\gamma}$), showed for all samples, can be described by the follows Eq. (3) [32]:

$$\tau = k \left(\dot{\gamma} \right)^{n-1} \qquad (3)$$

where *k* and *n* are consistency index and flow behavior index, respectively. From Eq. (3), we distinguish three behaviors as a function of the values of *n*: When *n* = 1, the viscosity of the system is independent of shear rate, the system presents a Newtonian behavior. In the second case *n* > 1, the system will exhibit shear-thickening behavior, for *n* < 1, a shear thinning behavior is observed.

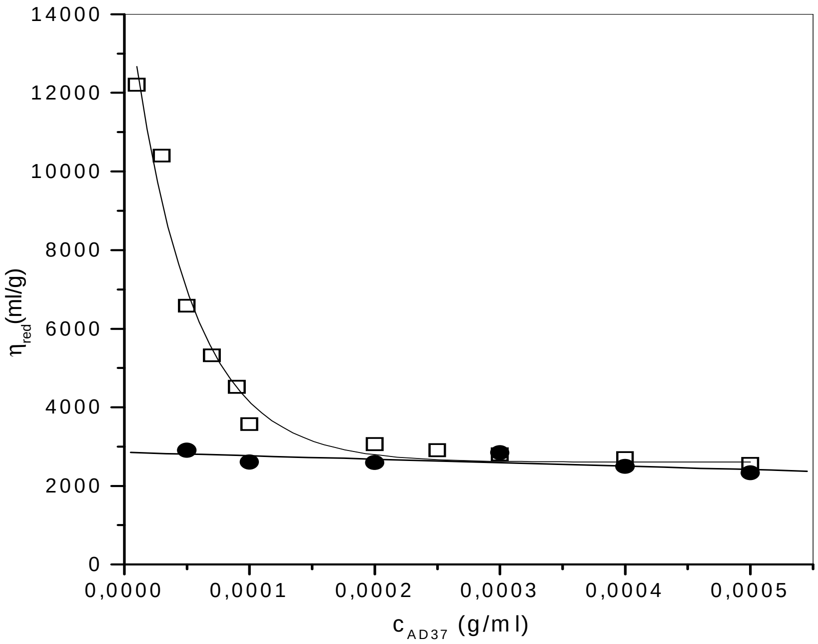

Figure 1: Reduced viscosity variation of the AD37 in absence and in presence of Nacl salt according to its concentration at 20 °C, □ AD37 alone; ● AD37+0.1M of NaCl

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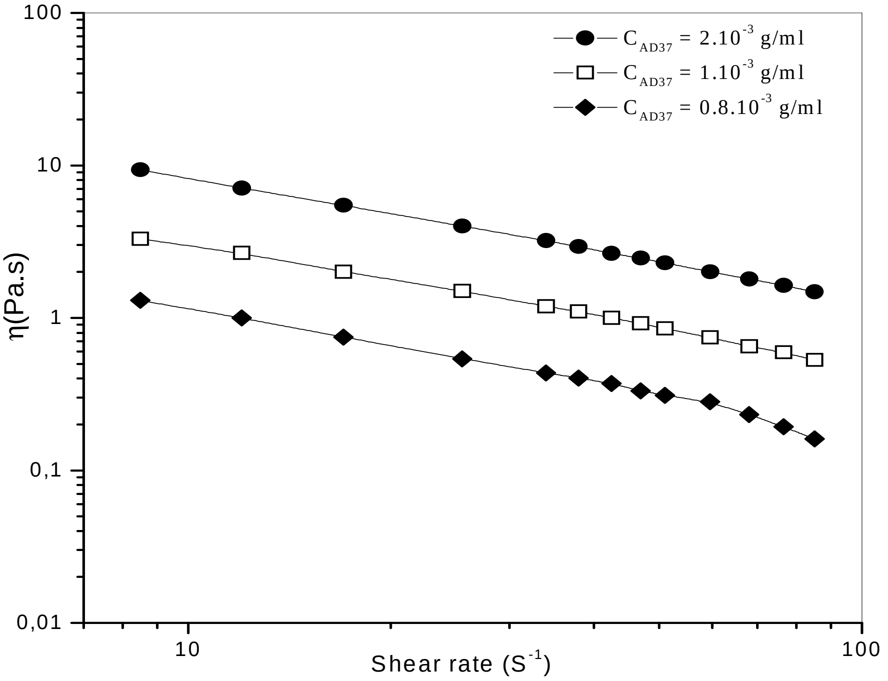

Figure 2: Viscosity variation of AD37 according to shear rate ($\dot{\gamma}$)

We distinguish three behaviors as a function of the values of *n*: When *n* = 1, the viscosity of the system is independent of shear rate, the system presents a Newtonian behavior. In the second case *n* > 1, the system will exhibit shear-thickening behavior, for *n* < 1, a shear thinning behavior is observed

3.3. Effect of the additive on the reduced viscosity of AD37 solutions

Figure 4 shows the effect of the addition of NaCl, DPC and P4VP on the reduced viscosity of AD37 solutions at fixed $C_{AD37}=10^{-5}$ g.ml^{-1}. We notice that the reduced viscosity of the polymer depends on both the additive and its concentration (Fig. 4). Indeed, the reduced viscosity variations are similar (the form exponential of the curves) for the all additive. The reduced viscosity of polyelectrolyte solution decrease when the additive concentration increases.

Addition of NaCl causes screening of the polymer charges. Consequently, a decrease in the reduced viscosity is observed. However, the reduced viscosity is strongly affected by addition DPC or P4VP in comparison with NaCl.

In the presence of DPC, we have to consider two effects. In the first case, the electrostatic interactions present between the anionic polymer (AD37) and the cationic surfactant. This interaction leads to a reduction of polymer charge number and, consequently, to a reduction in its viscosity. In the second case, the DPC chains can bind to the polyion chain cooperatively in the form of the so-called (polymer-induced) micelles [33, 34]. That is to say, the surfactant ions are not evenly distributed along the chain but they are rather localised in the form of smaller or bigger aggregates [34-37]. It's likely that polyelectrolyte chain encircles the surfactant micelles to some extent and this is accompanied by a further decrease both in dimensions and in viscosity [34].

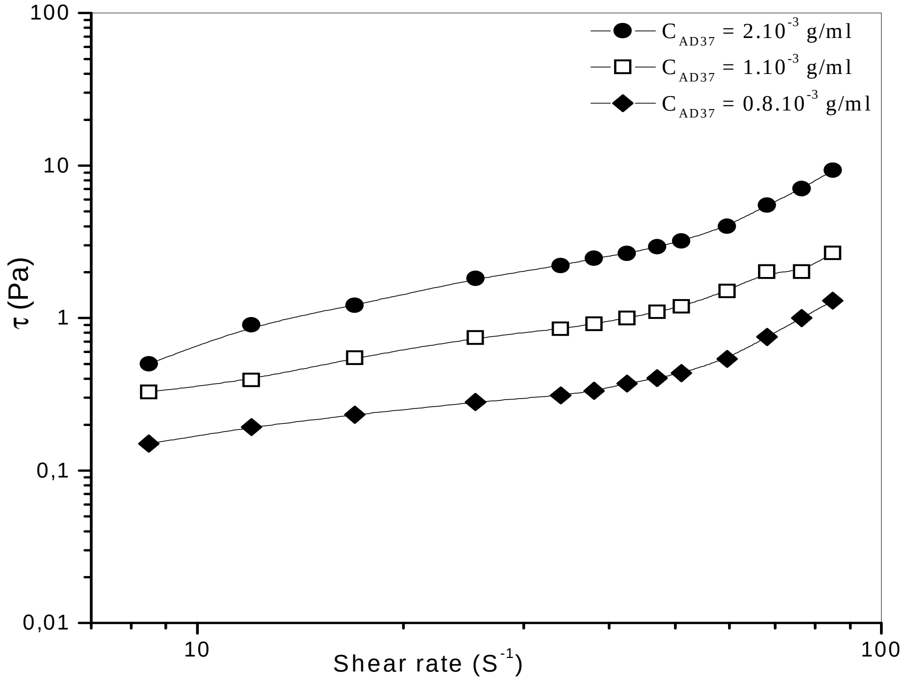

Figure 3: Shear stress variation of AD37 according to shear rate ($\dot{\gamma}$)

In the presence of P4VP, we have to study the interaction between oppositely charged polyelectrolytes. Indeed, the complexation of the AD37 with the P4VP is insured by acid–base interaction between the carboxylate function and the pyridinic nitrogen atom in a first place. In the second place the size of P4VP compared to NaCl and DPC. Mansri A. and al. [38] studied the viscosimetric behaviour of hydrolyzed polyacrylamide-poly(4-vinylpyridine) (AD37-P4VP) mixture in aqueous solution, at neutralization degree $\alpha = 1$. The result shows that the intermolecular electrostatic associations are favoured by increasing the P4VP concentration. Thus, mixtures rich in P4VP are characterized by a high decrease in the viscosity due to interpolymer complete complexation AD37-P4VP, leading to the totally contraction or collapse of the polymer chains.

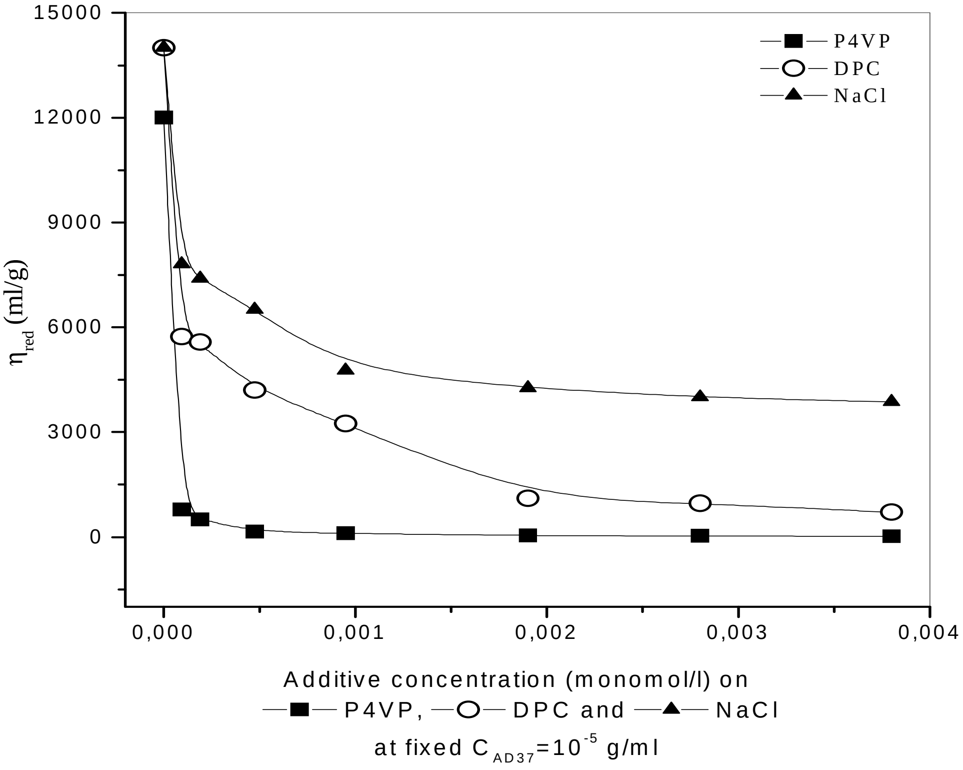

Figure 4: The effect of the addition of NaCl, DPC and P4VP on the reduced viscosity of AD37 solutions at $C_{AD37}=10^{-5}$ g.ml^{-1}.

4. Conclusion

The reduced viscosity and the rheological data for hydrolyzed polyacrylamide have been reported. A characteristic behavior of the viscosity of polyelectrolyte solutions is observed. For all samples (three concentrations of AD37: 0.8.10^{-3}g.ml^{-1}, 1.10^{-3} g.ml^{-1} and 2.10^{-3} g.ml^{-1}), as the shear rate increases, the typical behavior of pseudoplastic fluid is observed. The effect of NaCl, DPC and P4VP on the viscosimetric behavior of AD37 solution was investigated. It is apparent that the reduced viscosity of the polymer depends on both the additive and its concentration. Addition of NaCl causes screening of the polymer charges. Consequently, a decrease in the reduced viscosity is observed. However, the reduced viscosity is strongly affected by DPC in comparison with NaCl. Indeed, the viscosity of AD37 is very strongly influenced by the presence of P4VP in comparison with DPC.

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