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Interaction between weak neutralized polyelectrolyte complex polyacrylamide/poly(4-vinylpyridine) and sodium dodecylsulfate in saline medium

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ABSTRACT

The rheological behaviors of aqueous solutions of polyelectrolyte complex 27% hydrolyzed polyacrylamide [AD37]/poly(4-vinylpyridine) [P4VP] and charged surfactant, sodium dodecylsulfate (SDS), at neutralization degree $\alpha=0.1$, are reported. Viscosity variations of this system show a shear thinning behaviour for the strong shear rate. For low concentrations in P4VP, and at low shear rate, the fluid presents a Newtonian behaviour and tends to disappear when the concentration in P4VP increases ($4 \cdot 10^{-4}$ g/ml). The interaction of complex (AD37-P4VP) is favoured in the presence of the SDS where the electrostatic repulsions are dominant. Obtained results demonstrate that surfactant-complex polyelectrolyte interaction is governed by both electrostatic and hydrophobic interactions, and is cooperative in the presence of salt.

Key words: Polyelectrolyte, Anionic surfactant, Rheology, Neutralization degree, Complexation.

INTRODUCTION

Polyelectrolytes and surfactants are often found together in aqueous formulations of cosmetics, detergents, pharmaceuticals, and coatings to simultaneously control surface tension and rheology. Consequently, the interaction between polyelectrolytes and oppositely charged surfactants has been studied extensively [1-3]. These mixtures are frequently used in many industrial applications such as food, cosmetics, detergents, paints, etc. Polymers are used to control the rheology of the formulations and surfactants are used to control their surface properties (wettability, etc.) [4-9].

Interactions between charged polymers (polyelectrolytes) and charged surfactants have attracted increasing attention in the past decades, and rheological measurements were frequently used to get the information of the multi-component systems with polymer [10]. The change of rheological property of polymer solutions induced by surfactants with the same charge is very important for precise control of the polymers in practical applications [11]. At low concentrations, the surfactant binds individually to the polyelectrolyte through electrostatic interactions. A cooperative association occurs at the critical aggregation concentration, CAC, as the concentration is raised due to hydrophobic interactions between the surfactant tails [12]. The addition of a simple salt is also important since electrostatic interactions are partially screened when salt is present; the complexation depends not only on salt concentration, but also on the nature of salt ions, valence, etc.

Hydrolyzed polyacrylamide is a very important water-soluble polymer, which is used as a thickener or modifier for use in the formulations of tertiary oil recovery, drilling fluids, hydraulic fracturing and drag reduction [13-19].

Poly(4-vinylpyridine) is soluble only in highly polar solvents, reports on the solution properties of P4VP are very limited [20]. In a previous paper the complexation of the AD37 with the P4VP in aqueous solution was reported [21].

In this work, interactions in aqueous diluted solution between sodium dodecylsulfate (SDS) and the complex of polyelectrolyte (AD37/P4VP), for neutralization degree $\alpha = 0.1$, at 20°C were studied by rheological measurements. In the same way, the effect of salt (NaCl) on the behaviour of the mixture was quantified.

MATERIALS AND METHODS

Copolymer AD37 based on hydrolyzed acrylamide was provided from Rhône-Poulenc Company (France). Its content in carboxylate function is 27 % and is determined by ^{13}C NMR and potentiometry. Its weight-average molar mass is estimated to $2.8 \cdot 10^6$ g/mol by viscosity [21].

Poly(4-vinylpyridine), P4VP was synthesized in organic electrolytes and polyelectrolytes laboratory of Tlemcen University by free radical polymerisation, Its viscosimetric average molar mass is estimated to $3.42 \cdot 10^4$ g/mol. by viscosity [21].

Sodium dodecylsulfate (SDS) was supplied by Aldrich society. Its molecular weight is 288.38 g/mol. The rheological measurements were performed using a rheometer Bohlin type. Thus, we give the variation of dynamic viscosity as a function of shear rate from 0 to 200 S^{-1} to an imposed constraint and at $T = 20^\circ \text{C}$.

RESULTS AND DISCUSSION

Since the (AD37-P4VP-SDS) interaction yields structural changes in the solution, it can be supposed that these changes will be sensitive to the influence of shear rate in the rheological measurements.

Influence of interaction on the rheological characteristics of this system was investigated on AD37 solutions of 10^{-3} g/ml, and concentrations of P4VP ranging from $0.1 \cdot 10^{-4}$ g/ml to $4 \cdot 10^{-4}$ g/ml, SDS concentrations were taken of 10^{-2} g/ml and $2 \cdot 10^{-3}$ g/ml in the presence and absence of NaCl (0,1 N). The results are presented below.

Fig. (1.a) and (1.b) illustrate the evolution of dynamic viscosity as a function of shear rate in the presence and absence of NaCl at $T=20^\circ\text{C}$

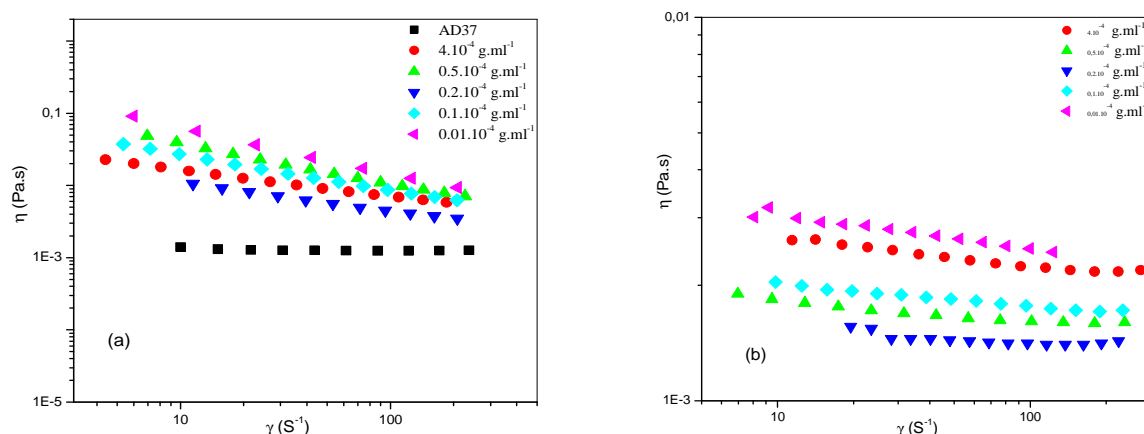


Fig. 1: Variation of dynamic viscosity of mixture (AD37-P4VP) according to the shear rate with: fixed $C_{\text{AD37}}=10^{-3}$ g/ml and for variable C_{P4VP} : (a) absence of NaCl, (b) in the presence of NaCl

A shear thinning behaviour is observed for mixture (AD37-P4VP), due to the orientation and the deformation of the complex formed in the flow. Viscosity decreases and takes the same pace. Thus, viscosity increases when the concentration in P4VP decreases. Indeed, the presence of the P4VP of small quantities increases the viscosity of the system (complex). In the presence of NaCl (Fig. 1.b), the variation between the curves becomes important according to the concentration in P4VP, and the values of viscosity are very low compared to the values recorded in (Fig. 1.a). A Newtonian behaviour is observed at low shear rate and for low concentrations in P4VP, followed by a reduction

in viscosity (shear thinning behaviour) due to the disorganization of the network thus formed. This strong shear rate dependence of the viscosity has previously been reported for many associative polymer systems of various natures [22]. For shear rate higher than 100 S^{-1} , a second Newtonian plate is observed for concentrations in P4VP higher than 10^{-5} g/ml . These various zones of viscosity variation represent structural changes of the solution under the shearing effect.

Fig. 2.a, 2.b, 2.c and 2.d, represent viscosity variation of the system (AD37-P4VP-SDS) according to the shear rate for a fixed concentration in AD37= 10^{-3} g/ml , and variable concentrations in P4VP and SDS, in presence and absence of NaCl.

In absence of NaCl, the viscosity of complex (AD37-P4VP) is modified by the presence of surfactant. (AD37-P4VP-SDS) System represents a shear thinning behaviour (Fig. 2. a et 2.c).

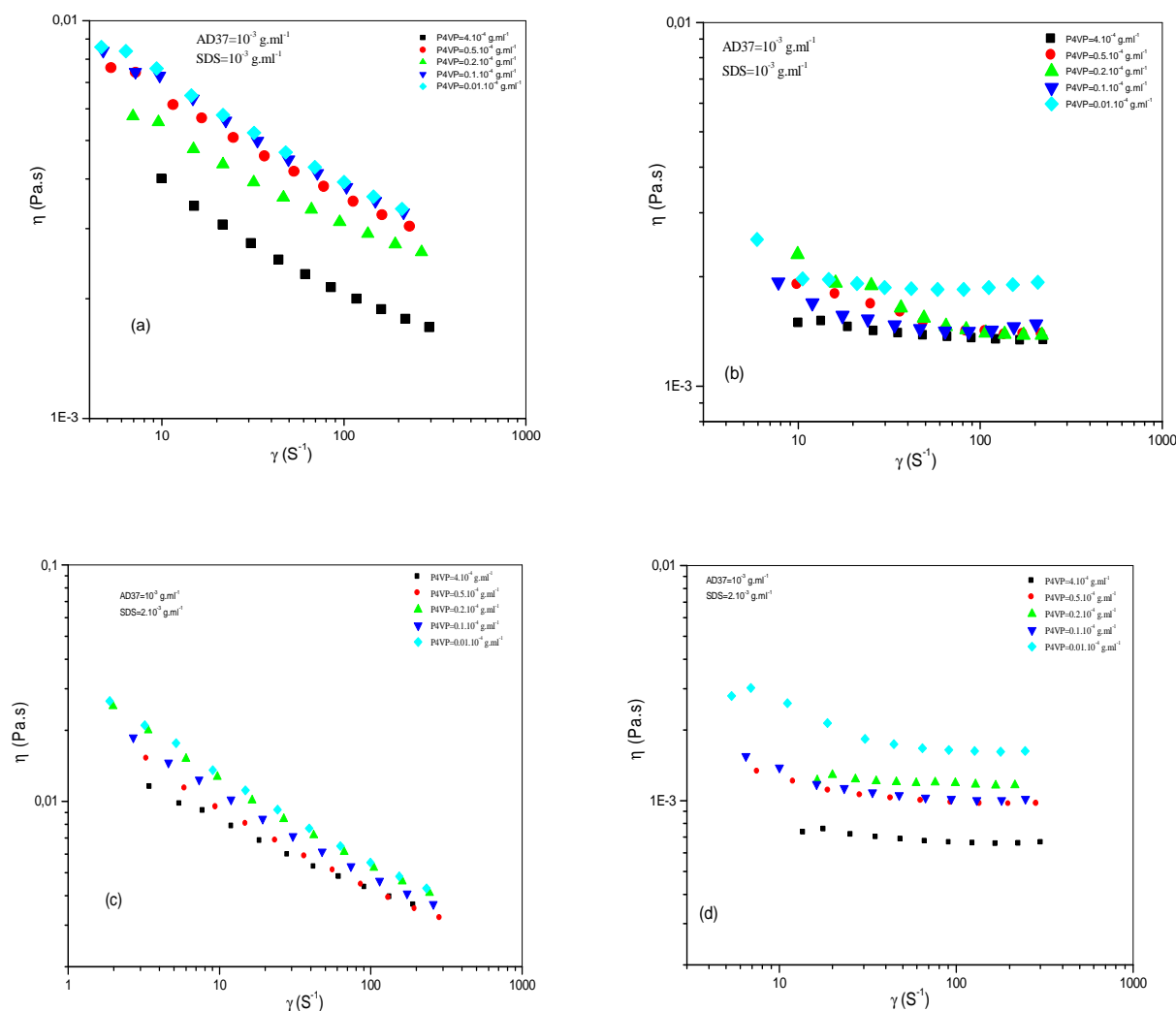


Fig. 2: Variation of (AD37-P4VP) viscosity, at fixed C_{AD37} ; C_{SDS} and C_{P4VP} variable, in presence and absence of salt.

For low concentrations in P4VP, and at low shear rate, the fluid presents a Newtonian behaviour (Fig.2.c), and which tends to disappear when the concentration in P4VP increases (4.10^{-4} g/ml). Indeed, viscosity increases when the concentration in SDS decreases (Fig. 2. a).

It should be noted that for an increase in SDS concentration of 5 times, viscosity values of the system decrease by a factor of 10, due to the strong interaction between the surfactant and the complex (electrostatic interaction) caused

by the electrostatic repulsion between the carboxylates ions of the AD37, and the sulphates ions of same signs present in the molecules of surfactant, followed by hydrophobic interactions, which generates the formation of polymer-surfactant micelles.

On the other hand, it was found starting from the results that the addition of NaCl involves a reduction in the viscosity of the system, which presents at very strong and at very low shear rates a Newtonian behaviour (Fig. 2.b and 2.d), the intermediate area can be described by a law of power (model of Ostwald de Waele).

CONCLUSION

This experimental study made it possible to include two different characters (Newtonian, and shear thinning behaviours) of studied system. (AD37/P4VP) and (AD37/P4VP/SDS) systems exhibit a shear thinning behaviour in the absence of salt. In presence of salt, and at low shear rates, a Newtonian behaviour is observed, it becomes shear thinning behaviour in the intermediate zone, then Newtonian at higher shear rate.

Complex formed between (AD37-P4VP) and the SDS are influenced by electrostatic interactions between not neutralized (COO⁻) ions and the sulphate ions of surfactant, followed by hydrophobic interactions between SDS chains and hydrophobic segments of the complex polyelectrolyte-polyelectrolyte. In the presence of NaCl, these interactions are influenced by electrostatic screening phenomenon.

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