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ORIGINAL CONTRIBUTION

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The influence of salt concentration on negative thixotropy in solutions of partially hydrolyzed polyacrylamide

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Abstract The influence of NaCl concentration on negative thixotropy in aqueous glycerol solutions of partially hydrolyzed polyacrylamide have been investigated. It was found that negative thixotropy type I (a slow increase in viscosity with time of shearing) sets in at higher critical shear rates when the salt is present. On the other hand, critical shear rates for negative thixotropy type II (a rapid increase in viscosity followed by viscosity oscillation) did not depend on the salt addition. Using the critical shear stress as a hydrodynamic criterion for the occurrence of negative thixotropy, a possible explanation of the behavior is proposed.

Key words Negative thixotropy – antithixotropy – shear thickening – polyacrylamide solutions – salt concentration

Introduction

Since the pioneer work of Eliassaf et al. [1] on negative thixotropy in solutions of poly(methacrylic acid) this rather unusual effect has been observed in aqueous solutions of other polymers, such as dextran [2, 3], poly(vinyl alcohol) [4] and partially hydrolyzed polyacrylamide [5–8]. Among them, negative thixotropic behavior of partially hydrolyzed polyacrylamide (PHPAA) attracts great attention due to many applications of its solutions in practice, for example, in oil enhanced recovery, viscosity control or as drag reducing agents.

With aqueous glycerol solutions of PHPAA two types of negative thixotropic effect were observed: at low shear rates a slow increase in viscosity with time of shearing to a limit (type I effect, Fig. 1a) and, at high shear rates, a steep increase in viscosity after some time of shearing followed by pronounced viscosity oscillation (type II effect, Fig. 1b) [8]. It was found that the effects occur at critical shear rates, $\dot{\gamma}_c$, which decreased with both PHPAA concentration and glycerol content [8]. As PHPAA is a polyelectrolyte whose properties strongly depend on ionic strength, the influence of simple salt on its negative thixotropic behavior was also studied. However, the results obtained in such investigations differ significantly. In our previous work [7, 9] an increase in $\dot{\gamma}_c$, with increasing NaCl content was observed. On the other hand, a slight decrease or near independence of $\dot{\gamma}_c$, on NaCl concentration was reported [6]. To elucidate these differences, we aimed at a more detailed study of the influence of NaCl concentration on the hydrodynamic conditions of the onset of negative thixotropy in solutions of PHPAA.

Experimental

The sample of partially hydrolyzed polyacrylamide ($\bar{M}_w = 7.10^6$, sodium salt, degree of hydrolysis, expressed as a percentage of amide groups converted to carboxyls, was 26%) was the same as in previous papers [7, 8]. The batch solutions containing 100, 190, 380, 750 and 1500 ppm of PHPAA in 85 wt. % aqueous glycerol were

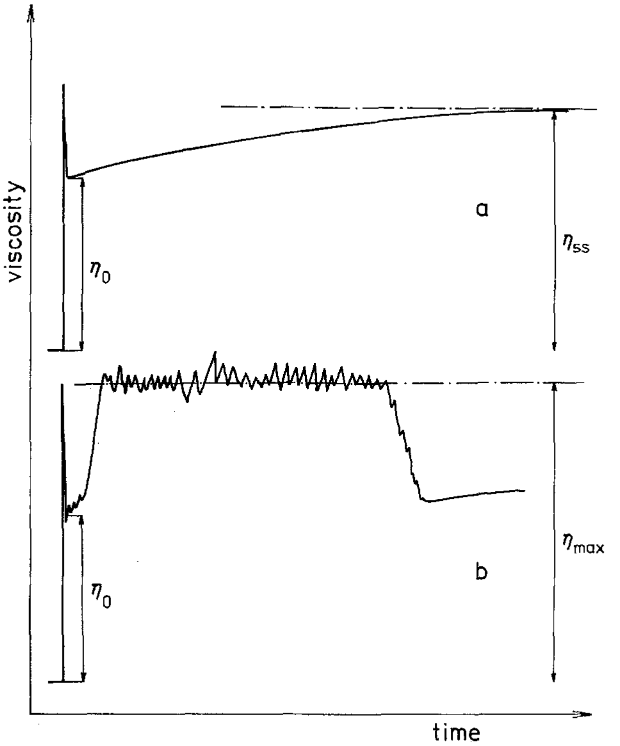

Fig.1 Schematic diagram of negative thixotropic behavior in aqueous glycerol solutions of PHPAA: a) type I, b) type II effect. η_o is the viscosity before inception of negative thixotropy, η_{ss} is the steady-state viscosity, η_{max} corresponds to maximum viscosity

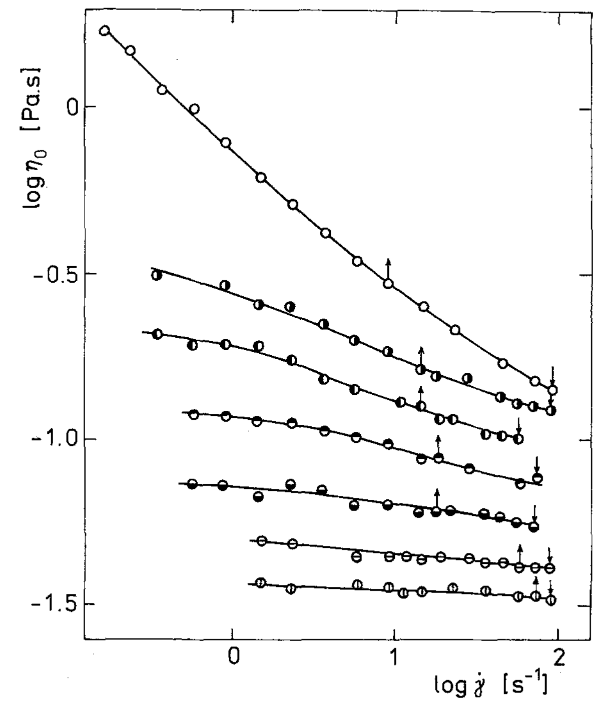

Fig. 2 Dependence of viscosity η_o on the shear rate $\dot{\gamma}$ at various NaCl concentrations (g/L): 0 (○), 0.5 (◑), 1.0 (◐), 2.0 (◓), 5.0 (◒), 10.0 (⊖), 20.0 (⦶). Arrows indicate critical shear rates for type I (↑) and type II (↓) effect, respectively. The corresponding curves were vertically shifted to avoid overlap. PHPAA concentration 380 ppm

prepared by dissolution of the polymer in water and subsequent glycerol addition. The mixtures were gently stirred with steel balls embedded in glass until homogeneous solutions were obtained. NaCl concentrations 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 g/L were obtained by the addition of solid NaCl (analytical grade). Due to a very high viscosity of low-salted PHPAA solutions the highest PHPAA concentration used (2500 ppm) was prepared at 20 g NaCl/L, only.

The time changes in viscosity were recorded at constant shear rates using a cone-and-plate Weissenberg rheogoniometer R 18 connected with a recording millivoltmeter. The shear stress, τ, was calculated according to the relation

$$\tau = \eta \cdot \dot{\gamma} \,, \qquad (1)$$

where η is viscosity and $\dot{\gamma}$ is the shear rate. The diameters of the cone and plate were 5 cm, the gap angle was 1.97°. When negative thixotropy set in, fresh samples were used. The viscosity η_0 before inception of the effects, steady-state viscosity η_{ss}, (for type I effect) and maximum viscosity η_{max} (for type II effect) were determined as shown in Fig. 1. All the measurements were performed at 25 ± 0.1 °C, 1 day after the preparation of the solutions. Further information on the experimental procedure is given elsewhere [8].

Results and discussion

The influence of NaCl on the critical shear rates

Although concentrations of PHPAA used were rather low, the viscosity of its non-salted solutions decreased rapidly with increasing shear rate, demonstrating pseudoplastic behavior (Fig. 2). With increasing NaCl concentration both viscosity of the solutions and their pseudoplasticity decreased, indicating a contraction of extended polymer coils caused by the screening effect of NaCl.

At the critical shear rate $\dot{\gamma}_c^I$, type I negative thixotropy appeared. With increasing NaCl concentration $\dot{\gamma}_c^I$ shifted to higher shear rates (Fig. 2) and, at the same time, the intensity of the effect expressed as a relative increase in viscosity during shearing, η_{ss}/η_o, slowly decreased from 1.15–1.10 (non-salted systems) to 1.03–1.05 (high NaCl contents). The increase in $\dot{\gamma}_c^I$ with NaCl concentration was observed at all PHPAA concentrations used but, with more diluted PHPAA solutions, the effect occurred at

Table 1 Critical shear rates $\dot{\gamma}_c^I$ at which type I negative thixotropy sets in

NaCl [g/L]	PHPAA [ppm] 100	190	380	750	1500	2500
0	90.9	36.1	9.1	9.1	1.43	–
0.5	143.8	36.1	14.3	14.3	2.28	–
1.0	228.2	72.2	14.3	14.3	2.28	–
2.0	–	90.9	18.2	18.1	3.62	–
5.0	–	90.9	18.2	22.8	7.2	–
10.0	–	–	57.3	28.7	5.7	–
20.0	–	–	72.2	45.5	7.2	2.38

higher shear velocities (Table 1). As a result of the behavior no negative thixotropic effects were observed at the lowest PHPAA concentrations, 100 and 190 ppm, above 1 and 5 g/L of NaCl respectively, even at the highest shear rate used $\dot{\gamma} = 1141\ s^{-1}$ (Table 1).

For 380–2500 ppm PHPAA solutions, type II negative thixotropy set in at shear rates $\dot{\gamma}_c^{II}$ which were higher than $\dot{\gamma}_c^I$ (Fig. 2). Similarly to type I effect, $\dot{\gamma}_c^{II}$ decreased with PHPAA concentration but, in contrast, did not depend on NaCl content within the experimental error (Table 2). Small effect of NaCl on this negative thixotropic behavior was also reflected in intensity of the effect η_{max}/η_o which practically did not depend on NaCl concentration (Fig. 3).

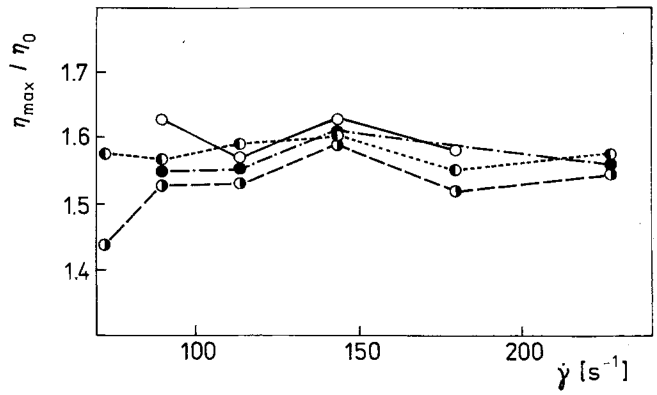

Fig. 3 Dependence of intensity (η_{max}/η_o) of type II negative thixotropy on shear rate $\dot{\gamma}$ at various NaCl concentrations (g/L): 0 (○), 2 (◑), 5 (◐), 20 (●). PHPAA concentration 380 ppm

The influence of NaCl on the critical shear stress

The origin of negative thixotropy in polymer solutions remains still unclear. It is assumed that the effect is caused by the association of macromolecules activated by their deformation and orientation in the shear field. As the frictional forces acting on macromolecules in flow are proportional to the shear stress rather than to shear rate, a critical shear stress was proposed as a more general hydrodynamic criterion for the occurrence of negative thixotropy [10].

The critical shear stresses τ_c^I and τ_c^{II} for negative thixotropy type I and II, respectively, calculated from Eq. (1) using values $\dot{\gamma}_c^I$ and $\dot{\gamma}_c^{II}$ and the corresponding viscosities η_o, changed with NaCl concentration in a characteristic way (Fig. 4). It has been found that at the lowest PHPAA concentrations (100 and 190 ppm) τ_c^I increased rapidly with NaCl concentration (Fig. 4a) while in more concentrated solutions τ_c^I first decreased to a shallow minimum and then rose (380–750 ppm, Fig. 4b) or decreased to a limit (1500 ppm, Fig. 4c). The critical shear stress τ_c^{II} varied with NaCl content in a similar manner (Fig. 5). In this case, however, the decrease to a minimum was steeper and the following increase was slower than in the case of τ_c^I.

Table 2 Critical shear rates $\dot{\gamma}_c^{II}$ at which type II negative thixotropy sets in

NaCl [g/L]	PHPAA [ppm] 380	750	1500	2500
0	90.9	57.3	28.7	–
0.5	90.9	90.9	22.8	–
1.0	57.3	57.3	22.9	–
2.0	72.2	57.3	22.8	–
5.0	72.2	57.3	22.8	–
10.0	90.9	72.2	22.8	–
20.0	90.9	72.2	22.8	9.1

One could expect that reduction in size of PHPAA coils caused by the screening effect of low-molecular-weight ions should increase critical shear stresses. The decrease in chain dimensions reduces the possibility of chain overlap and, thus, acts against the occurrence of negative thixotropy [11]. Moreover, for compact polymer coils higher frictional forces must be applied to reach a certain critical deformation and orientation of coils necessary for the formation of a negative thixotropic structure. For that reason, a decrease in chain dimensions caused by NaCl addition should suppress the effect and shift critical shear stresses to their higher values.

Colloid & Polymer Science, Vol. 273, No. 5 (1995)

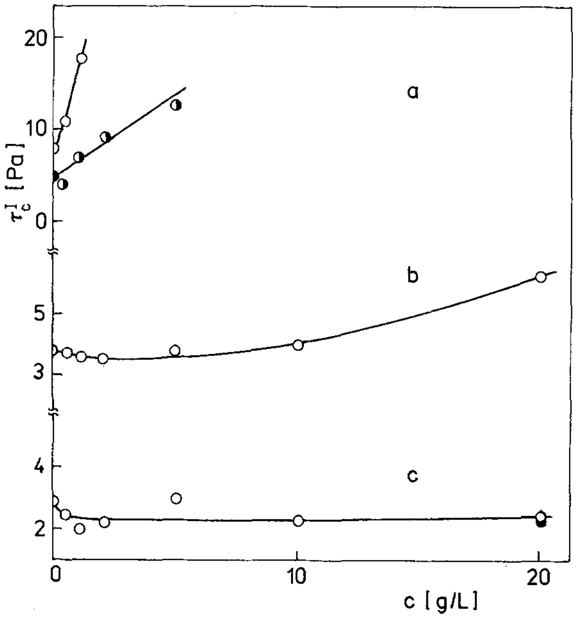

Fig. 4 Dependence on NaCl concentration of the critical shear stress τ_c^I at which type I negative thixotropy sets in. PHPAA concentration: a) 100 (○), 190 (◑); b)750; c) 1500 (○) and 2500 ppm (●)

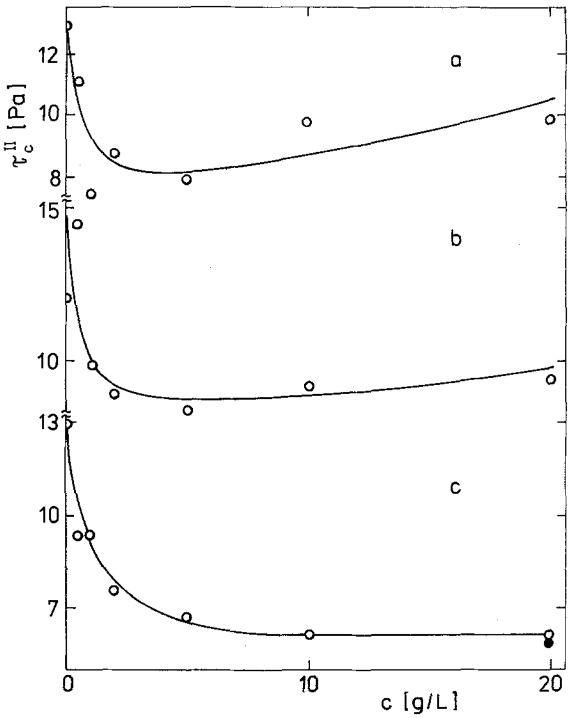

Fig. 5 Dependence on NaCl concentration of the critical shear stress τ_c^{II} at which type II negative thixotropy sets in. PHPAA concentration: a) 380, b) 750, c) 1500 (○) and 2500 ppm (●)

On the other hand, a decrease in intermolecular electrostatic repulsions should enhance the affinity of PHPAA macromolecules for association in thermodynamically poor solvents such as aqueous glycerol [7] and, hence, it should cause critical shear stress to decrease [8].

We believe that the shape of the dependences τ_c^I and τ_c^{II} vs. NaCl concentration (Figs. 4 and 5) results from superposition of these two effects. At small PHPAA concentrations, 100 and 190 ppm, the decrease in chain dimensions became a dominant factor leading to an increase in τ_c^I with NaCl concentration or, at the highest NaCl content, to a complete suppression of the effect. At 380 and 750 ppm, an increased ability of PHPAA to associate in shear field prevails over the decrease in chain dimensions which is reflected in the initial decrease in the critical shear stresses. At higher NaCl concentrations, however, the decrease in chain dimensions is more pronounced which increases critical shear stress. On the other hand, a 1500 ppm PHPAA concentration is high enough to fulfil the condition of sufficient chain overlap even at the highest NaCl concentrations. Consequently, the critical shear stresses only decreased to a limit. In this case the screening effect of NaCl led obviously to the same results as a reduction in number of electrical charges due to decreasing degree of ionization [8].

According to Eq. (1) the critical shear rate depends on the critical shear stress and is inversely proportional to solution viscosity. As the τ_c^I values steeply increased with NaCl concentration (Fig. 4a) or their change was only small (Fig. 4b, c) while viscosity of the solutions decreased rapidly, critical shear rates $\dot{\gamma}_c^I$ increased with NaCl concentration. On the other hand, the decrease in both τ_c^{II} and viscosity at low NaCl concentrations (Fig. 5) might compensate, which would lead to $\dot{\gamma}_c^{II}$ independent on NaCl concentration. At more salted solutions the changes in both quantities with NaCl concentration were rather small which caused values of $\dot{\gamma}_c^{II}$ virtually independent of NaCl content (Table 2).

Conclusion

Negative thixotropic effects in aqueous glycerol solutions of partially hydrolyzed polyacrylamide respond to NaCl concentration in a very different manner. Type I effect characterized by a slow increase in viscosity with time of shearing could be observed only at higher shear rates and its intensity decreased after NaCl addition. On the other hand, both critical shear rates and intensity of type II effect observed as a rapid increase in viscosity accompanied by its oscillation, did not change with NaCl concentration.

Considering critical shear stress as a more general hydrodynamic critierion for the occurrence of the effects, it seemed that independence of critical shear rates for type II negative thixotropy on NaCl concentration is caused by a simultaneous decrease in both critical shear stress and viscosity and, at higher NaCl concentrations, by small variations of the quantities. In some cases, however, critical shear stress might decrease with NaCl concentration more rapidly than the corresponding viscosity which results in a decrease in the critical shear rates with NaCl concentration as observed in [6].

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