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# Comparative Studies of Rheological Properties of Polyacrylamide and Partially Hydrolyzed Polyacrylamide Solutions

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**ABSTRACT:** The present work is concerned with experimental results of rheological characteristics of polyacrylamide (PAM) and of partially hydrolyzed polyacrylamide (HPAM) (degree of hydrolysis up to 80%) in aqueous and aqueous/sodium chloride solutions with changing experimental conditions such as polymer concentration, temperature, solvent quality, and shear rate applied. It has been observed that the all-aqueous and aqueous/NaCl solution of PAM and of HPAM exhibited the non-Newtonian behavior with shear-thinning and shear-thickening areas. The onset of shear-thickening at  $\dot{\gamma} = \dot{\gamma}_c$  depends mainly on the degree of HPAM

hydrolysis, as well as on solution concentration, temperature, solvent quality, and polymer molecular weight. Rheological parameters from power law (Ostwald de Waele model) and activation energy of viscous flow ( $E_a$ ) are determined and discussed. The changes in apparent shear viscosity during aging of solutions of PAM and HPAM are also described. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2235–2241, 2007

**Key words:** polyacrylamide; shear-thickening behavior; rheology; apparent viscosity

## INTRODUCTION

Natural and synthetic high molecular weight compounds are currently used as thickening agents in paper industry, food industry, enhanced oil recovery processes,<sup>1</sup> and aircraft fuel handling.<sup>2</sup> Polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) are synthetic, water-soluble polymers, showing unique shear-thickening properties. HPAM is a copolymer of acrylamide and sodium acrylate. The degree of hydrolysis is defined as the number  $Y$  of carboxyl residues ( $\text{COO}^-$ ) replacing the amide groups ( $\text{CONH}_2$ ) ( $X$ ) over the total number of the macromolecular residues  $Y/(X + Y)$ . HPAM is an anionic polyelectrolyte, and in aqueous solution, the electrostatic interactions are weakly screened; hence, the polyelectrolytic effect of HPAM is observed. Acrylamide based on homo- and copolymers have been used as flocculents, dispersants, retention aids, steric stabilizers, and associate thickeners in areas as diverse as municipal and industrial waste water treatment, mineral flotation, paper making, oil and coal refineries, and emulsion polymerization reactions, etc.<sup>3,4</sup>

Yang et al.<sup>5–7</sup> have presented the investigations of rheological properties of PAM in aqueous solutions.

These investigations have shown the influence of the temperature, concentration,<sup>5,6</sup> and addition of metal ions<sup>7</sup> on the rheological behavior of low concentration PAM solutions. The shear-thickening behavior in these PAM solutions has not been discussed. Recently, Hamley and coworkers<sup>8</sup> have reported the results of the rheological properties of PAM and hydrophobically modified PAM.

Studies of the rheological properties of HPAM with relatively high molecular weights in glycerol/water mixtures and in aqueous/sodium chloride solution have been reported.<sup>1,9–12</sup> These studies have shown the influence of the glycerol content in the solvent mixture (HPAM of DH = 1.5%,<sup>1</sup> DH = 25%,<sup>9</sup> DH = 40%<sup>10</sup>) and of the addition of simple electrolyte and variation of temperature (HPAM of DH = 2%<sup>11</sup>) upon the shear-thickening behavior of HPAM solutions. The authors<sup>1,9–12</sup> did not consider the influence of the hydrolysis degree of HPAM on the flow curves.

In the present article the rheological studies of solutions of PAM and of HPAM samples with varying hydrolysis degrees (DH = 0, 1.5, 20, 80) are widely described. The measurements were carried out with changing sample properties such as degree of hydrolysis, molecular weight, and with changing experimental conditions such as polymer concentration, solvent quality, temperature, shear rate, and storage time. Moreover, for the all investigated samples, the mathematical interpretation of relationship between the apparent viscosity  $\eta_a$  and the shear rate  $\dot{\gamma}$ ,

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TABLE I  
Characteristics of Samples

Sample no.	Polymer	$\overline{M}_v$ ( $10^{-6}$ g/mol)	DH (%)	Solvent	$c$ (%)	$\dot{\gamma}_c$ ( $s^{-1}$ )	Source
A: Polymer samples (this study)							
1	PAM	5	0	1% NaCl	1	800	Acros
2	HPAM (1.5)	15	1.5 <sup>a</sup>	1% NaCl	0.5	500	Aldrich
3	HPAM (20)	0.15	20 <sup>b</sup>	1% NaCl	1.5	380	Aldrich
4	HPAM (80)	0.2	80 <sup>b</sup>	2% NaCl	2	700	Aldrich
B: HPAM Samples (Studies of Other Authors <sup>1,9-11</sup> )							
5	HPAM <sup>11</sup>	5	$\sim 2$	1% NaCl	1	300	
6	HPAM <sup>9</sup>	7	25	Water/80% glycerol/2% NaCl	0.034	30	
7	HPAM <sup>1</sup>	5	1.5	Water/75% glycerol/2% NaCl	0.2	300	
8	HPAM <sup>10</sup>	10	40	Water/75% glycerol/3% NaCl	0.08	100	

DH is the degree of hydrolysis of HPAM;  $c$ , the polymer concentration;  $\dot{\gamma}_c$ , the critical value of shear rate.

<sup>a</sup> Poly(acrylamide-co-acrylic acid).

<sup>b</sup> Poly(acrylamide-co-acrylic acid), sodium salt.

according to the Ostwald de Waele model,<sup>13</sup> was carried out. Energy of viscous flow ( $E_a$ ) has also been determined and discussed.

## EXPERIMENTAL

### Materials

The characteristics of polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) samples are given in Table I(A).

Distilled water and aqueous/NaCl solution ( $c = 1\%$ , m/m) were used as solvent.

### Measurements

The solutions of PAM ( $c = 1\%$ ) and HPAM ( $c$ , 0.5–2%) were prepared by shaking the polymer with the solvent at room temperature. Flow measurements were carried out using a rotary viscometer Bohlin Visco 88 with concentric cylinder over a range of temperature from 293 to 318 K and with shear rates up to  $1220 s^{-1}$ . The obtained solutions were transparent and stable, as the reproducibility of the flow curves was very high.

### Data analysis

A useful form of expressing the flow behavior is the power law relationship of the Ostwald de Waele model<sup>13</sup>:

$$\tau = k\dot{\gamma}^n \quad \text{and} \quad \eta = \tau/\dot{\gamma} = k\dot{\gamma}^{n-1} \quad (1)$$

where  $\tau$  is the shear stress,  $\dot{\gamma}$  is the shear rate,  $\eta$  is the shear viscosity,  $n$  and  $k$  are constants, known as the non-Newtonian index and the consistency index, respectively. From the equation it follows that if  $n$  is unity, then  $k$  is identical to  $\eta$  and eq. (1) appears as Newton's law.

Activation energy of viscous flow ( $E_a$ ) was calculated with the Arrhenius equation:

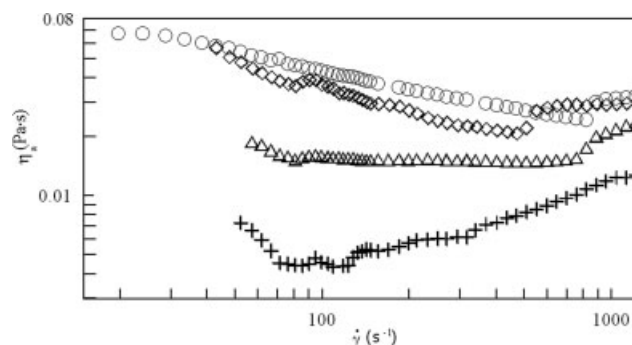
$$\eta_a = A_o \exp(E_a/RT) \quad (2)$$

where  $A_o$  is a preexponential parameter and  $E_a$  is the activation energy of viscous flow.

## RESULTS AND DISCUSSION

### Shear-thinning and shear-thickening behavior

The viscosity curves for solutions of PAM and HPAM in 1 and 2% aqueous NaCl are presented in Figure 1. The solutions of PAM and HPAM samples used in the present investigation behave as non-Newtonian fluids. The viscosity curves for PAM and HPAM solutions may be roughly divided into two parts: a region below the critical value of shear rate,  $\dot{\gamma}_c$ , where a relatively large shear-thinning effect is observed, and a second region above the critical value of shear rate,  $\dot{\gamma}_c$ , in which the shear-thickening behavior occurs. Thus, the critical value of shear rate,  $\dot{\gamma}_c$ , is the shear rate above which the onset of solution shear-thickening is



**Figure 1** Apparent shear viscosity versus shear rate of PAM and HPAM in aqueous/NaCl solution,  $T = 298$  K.  $\circ$ , PAM  $c = 1.0\%$ ;  $\diamond$ , HPAM (1.5)  $c = 0.5\%$ ;  $+$ , HPAM (20)  $c = 1.5\%$ ;  $\triangle$ , HPAM (80)  $c = 2.0\%$ .

observed. In the first region ( $\dot{\gamma} < \dot{\gamma}_c$ ) the decrease of the viscosity with shear rate (shear-thinning behavior) is mainly related to the orientation of macromolecules along the streamline of flow and to the disentanglement of macromolecules with the increasing shear force.<sup>12,13</sup> The phenomenon of shear-thickening may be related to a change of the macromolecule conformation induced by flow (deformation and associations of macromolecules).<sup>9,12</sup> A temporary network or entanglements of the unfolded macromolecules could possibly be formed under flow conditions. For  $\dot{\gamma} > \dot{\gamma}_c$ , a large number of polymer chains in the unfolded conformation will participate in the formation of the temporary network, which gives rise to an increase in the viscosity of the polymer solution. When the shear is switched off, the temporary network will decay, as the chains return to the more thermodynamic stable coil state. In the case of HPAM solutions, the electrostatic interactions participate in the shear-thickening phenomenon. The shear forces may disturb the screening of electrostatic charges and, as a consequence, the repulsive forces between negative charges in HPAM molecules may cause the increase of  $\eta_a$  in the shear-thickening region.

For the solution of HPAM samples of high degree of hydrolysis ( $\text{DH} \geq 20\%$ ) in the region at relatively high shear rate (cf. Fig. 1,  $150 < \dot{\gamma} \text{ (s}^{-1}\text{)} < 300$  for HPAM (20) and  $100 < \dot{\gamma} \text{ (s}^{-1}\text{)} < 700$  for HPAM (80), the compensation of orientation and disentanglement effects with the effects of deformation and association takes place. As a result, at some ranges of  $\dot{\gamma}$  the solutions HPAM (20) and HPAM (80) show Newtonian behavior ( $n \cong 1.0$ , cf. Table II).

### Influence of the degree of hydrolysis

The values of  $\dot{\gamma}_c$  for HPAM samples having various hydrolysis degrees and various molecular weights, obtained on the basis of our results, are presented in Table I(A). For comparison and discussion, the results obtained by other authors<sup>1,9–11</sup> are shown in Table I(B).

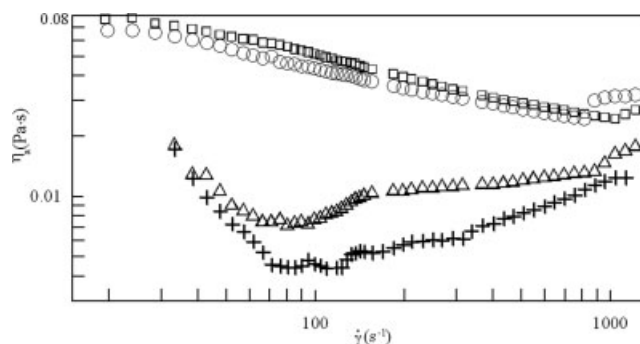
As can be observed, in the case of Samples 1 [Table I(A)] and 5 [Table I(B)] (of the same molecular weight, solution concentration, and solvent: aqueous/1% NaCl), the increase of the hydrolysis degree from 0 to 2% causes decrease of  $\dot{\gamma}_c$  from 800 to 300  $\text{s}^{-1}$ . Thus, the increase of the degree of hydrolysis causes the shear-thickening behavior of HPAM solutions to be observed at a lower value of  $\dot{\gamma}_c$ . The same is observed for Samples 6 and 7 [Table I(B)] (the same solvent and similar molecular weight), where the increase of the hydrolysis degree causes a pronounced decrease of  $\dot{\gamma}_c$  (from 300 to 30  $\text{s}^{-1}$ ). Additionally, in the case of Sample 6 [Table I(B)] the decrease of  $\dot{\gamma}_c$  is also caused by the very low solution concentration of this sample.

From the results shown in Figure 1 it is seen that the region of shear-thinning behavior increases with the decrease of the degree of hydrolysis of HPAM. Thus, the region of shear-thickening is relatively small for the solution of PAM and HPAM of low degree of hydrolysis: Sample 1 ( $\text{DH} \approx 0$ , cf. the following explanation) and Sample 2 ( $\text{DH} = 1.5$ ), in comparison with HPAM (20). An opposite trend is observed in the case of HPAM solutions of relatively high degree of hydrolysis ( $\text{DH} = 20\%$ , Sample 3). Hence, HPAM solutions of  $\text{DH} = 20\%$  show a narrow shear-thinning region below the value of  $\dot{\gamma}_c$  and a wide shear-thickening region above  $\dot{\gamma}_c$ . Similar direction of changes were observed by Ghannam,<sup>11</sup> for the HPAM [Sample 5, Table I(B)], and by Wang et al.,<sup>10</sup> for HPAM [Sample 8, Table I(B)]. Their results also show that the narrow shear-thinning region and the  $\dot{\gamma}_c$  values are found at 300 and 100  $\text{s}^{-1}$ , respectively.

The shear-thickening phenomenon for the current PAM and HPAM solutions was observed both in aqueous solution and in aqueous/NaCl solutions. Figure 2 shows the viscosity curves of apparent shear viscosity versus shear rate for PAM and HPAM (20) aqueous solutions, in comparison with aqueous/NaCl solutions, at 298 K. In the case of PAM solutions the apparent viscosity in aqueous solution and in

TABLE II  
Rheological Parameters for PAM and HPAM in Aqueous/NaCl ( $c = 1\%$ )  
Solution at 298 K

	Range, $\dot{\gamma} \text{ (s}^{-1}\text{)}$	$n$ [eq. (1)]	$k$ [eq. (1)]	$R^2$
PAM [ $c = 1\%$ ]	19–400	0.70	0.18	0.999
	400–820	0.76	0.12	1.00
	885–1220	1.20	$9 \times 10^{-3}$	0.999
HPAM (1.5) [ $c = 0.5\%$ ]	19–100	0.61	0.21	0.984
	100–550	0.70	0.19	1.00
	600–1220	1.62	$4 \times 10^{-4}$	0.994
HPAM (20) [ $c = 1.5\%$ ]	147–300	1.02	$5 \times 10^{-3}$	0.991
	300–800	1.54	$3 \times 10^{-4}$	0.997
	800–1220	1.53	$3 \times 10^{-4}$	1.00
HPAM (80) [ $c = 2\%$ ]	100–500	1.1	$6 \times 10^{-3}$	0.994
	600–1220	1.74	1.24	1.00



**Figure 2** Apparent shear viscosity versus shear rate of PAM and HPAM solutions,  $T = 298$  K.  $\circ$ , 1.0% PAM in aqueous/NaCl ( $c = 1\%$ );  $\square$ , 1.0% PAM in  $H_2O$ ;  $+$ , 1.5% HPAM (20) in aqueous/NaCl ( $c = 1\%$ );  $\triangle$ , 1.5% HPAM (20) in  $H_2O$ .

aqueous/NaCl solution are comparable in the range of  $19 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 1220$ . However, the critical shear rate,  $\dot{\gamma}_c$ , for aqueous PAM solution is observed at  $1034 \text{ s}^{-1}$ , and by adding NaCl to aqueous PAM solution,  $\dot{\gamma}_c$  shifts to a lower shear rate of  $800 \text{ s}^{-1}$  and does not change with the change of NaCl concentration ( $1\% \leq c_{\text{NaCl}} \leq 2\%$ ). The value of the  $n$  parameter calculated for aqueous solution of PAM is 1.59 at  $298 \text{ K}$  ( $1030 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 1220$ ). This value is higher than the value of the  $n$  parameter for the aqueous/NaCl solution ( $n = 1.20$ ). Thus, the decrease of the  $\dot{\gamma}_c$  value and the increase of the  $n$  parameter of PAM may be an indication that the neutral polyacrylamide may contain a very low amount of carboxylic groups caused by its hydrolysis in water.

Aqueous solution of HPAM (20) indicates higher apparent viscosity than the apparent viscosity of HPAM (20) aqueous/NaCl solution. In water solution of HPAM (20) for shear rates in the range of  $104\text{--}184 \text{ s}^{-1}$  and above  $900 \text{ s}^{-1}$  the apparent viscosity increases rapidly. The values of the  $n$  parameter are 1.54 and 1.63, respectively.

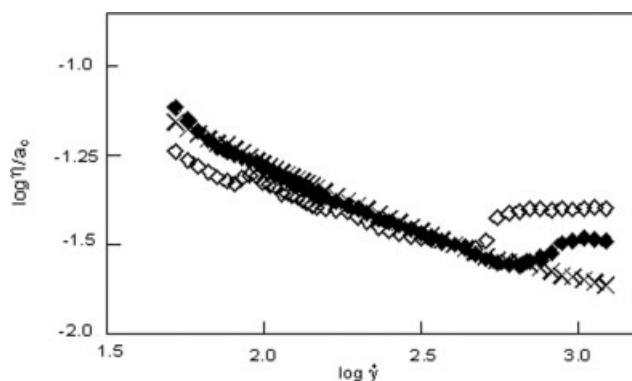
From the results shown in Figure 2 it is evident that the behavior of PAM solutions is different in comparison with HPAM (20) in aqueous and aqueous/NaCl solutions. The reason is that these two commercially samples differ in their molecular structure. PAM sample is a nonionic polymer, (disregarding hydrolysis in water) whereas the HPAM (20) contains ionic groups. Hence, in aqueous solution the polyelectrolytic effect of HPAM is observed. So, the addition of NaCl to HPAM (20) solution decreases the apparent viscosity of HPAM solution and influences the course of viscosity curve shown in Figure 2. In the aqueous solution of a polyelectrolyte, the macromolecules are stretched because of the electrostatic repulsive forces between the negative charges on the carboxylic groups.<sup>1,11</sup> The addition of salt to the solution induces the increase of solution ionic strength and screens the electrostatic charges. Then the macromolecule

conformation reduces to the statistical coil conformation. As a consequence, a decrease of the HPAM (20) apparent viscosity in aqueous/NaCl solution in comparison with aqueous solution is observed (Fig. 2).

### Influence of polymer concentration

The influence of polymer concentration upon the apparent viscosity versus shear rate relationship for HPAM (1.5) in aqueous/NaCl solution at  $298 \text{ K}$  is shown in Figure 3.

It can be observed that the value of  $\dot{\gamma}_c$  shifts to higher shear rates with the increase in polymer concentration, i.e., for 0.5% HPAM (1.5)  $\dot{\gamma}_c = 500 \text{ s}^{-1}$  and for 0.8% HPAM (1.5)  $\dot{\gamma}_c = 600 \text{ s}^{-1}$ . In the case of 1% HPAM (1.5) solution ( $\times$  at Fig. 3), the shear-thickening behavior in the investigated range of shear rate ( $n = 0.70$  for shear rate from  $19$  to  $1220 \text{ s}^{-1}$ , at  $298 \text{ K}$ ) was not observed. The master curve (Fig. 3) is obtained by vertical shifting of viscosity curves of the HPAM (1.5) solutions at different concentrations: 0.5, 0.8, and 1%. At decreasing concentration of HPAM (1.5) solution the viscosity curves present a more pronounced non-Newtonian behavior. Only the shear-thinning behavior (not shown here) occurs also for the 2% PAM solution in the range of shear rates  $19\text{--}1220 \text{ s}^{-1}$ . In the case of the investigated HPAM (20) solutions, the region of the shear-thickening behavior decreases with the increase in polymer concentration. We observed, for example, that 6% solution of HPAM (20) at  $298 \text{ K}$  and  $300 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 1220$  showed the flow pattern close to the Newtonian one ( $n = 1.05$ ). Such behavior is caused by an increase in the polymer concentration, which influences the increase of entanglements of macromolecular chains, leading to the broadening of the shear-thinning region. The obtained results confirm the results of the studies of other authors<sup>1,9</sup> and show that shear-thickening properties are usually observed at a relatively low polymer concentration.



**Figure 3** Master curve  $\log \eta/a_c$  versus  $\log \dot{\gamma}$  of HPAM (1.5) in aqueous/NaCl ( $c = 1\%$ ) solution, at various concentrations:  $\diamond$ ,  $c = 0.5\%$ ;  $\blacklozenge$ ,  $c = 0.8\%$ ;  $\times$ ,  $c = 1\%$  at  $T = 298 \text{ K}$ . Vertical shifting by  $a_c = \eta_c/\eta_{c_0}$ ,  $c_0 = 0.5\%$  (reference concentration).

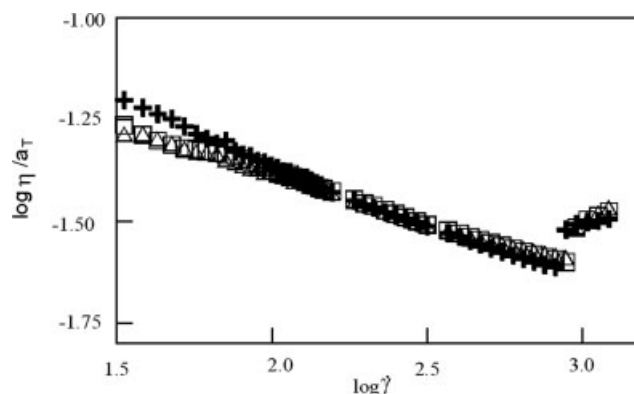
### Influence of molecular weight

It is well known<sup>14</sup> that polymer chains are highly coiled in equilibrium state and there is a high degree of both inter- and intrachain entanglement. When a stress is applied, the chains tend to become aligned and disentangled. We would expect the resistance to flow and hence viscosity to increase as the chain length ( $Z$ ) increases, which occurs in practice. The relationship between  $\eta_0$  and  $Z$  can be written as  $\eta_0 = K_1 Z$  for  $Z < Z_c$  and  $\eta_0 = K_2 Z^{3.4}$  for  $Z > Z_c$ , where  $K_1$  and  $K_2$  are temperature-dependent constants,  $\eta_0$  is the viscosity at  $\dot{\gamma} \rightarrow 0$ , and  $Z_c$  is the critical chain length, at which the abrupt change in slope occurs for plot of the relationship  $\eta_0$  versus  $Z$ . As chain length increases, the number of entanglements increases sharply and we obtain a very strong dependence between  $\eta_0$  and  $Z$ .

The influence of molecular weight on  $\dot{\gamma}_c$  may be roughly deduced by comparison of Sample 2 [Table I(A)] with Sample 5 and eventually Sample 7 [Table I(B)]: the increase of molecular weight causes the increase of  $\dot{\gamma}_c$  value. Such a behavior is caused by an increase in the chain length, which influences the increase of entanglement of chain, leading to the broadening of shear-thinning region; hence, the shift of shear-thickening phenomenon to higher values of  $\dot{\gamma}$  is observed.

### Rheological parameters

Flow properties of the used PAM and HPAM solutions obey the Ostwald de Waele model [eq. (1)]. Characteristic parameters were determined in three regions of shear rate  $\dot{\gamma}$ , as is presented in Table II. For all the investigated polymer solutions (PAM and HPAM of  $1.5 \leq \text{DH} \leq 80$ ) the power law model provides a good fit to the data all over the range of shear rates used. The value of the  $n$  parameter from the Ostwald de Waele model indicates Newtonian flow behavior ( $n = 1$ ) or non-Newtonian flow behavior ( $n \neq 1$ ). The value of  $n < 1$  indicates the shear-thinning effect, and the value of  $n > 1$  implies the shear-thickening behavior. In the case of the PAM solutions in the region of  $400 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 800$ ,  $n = 0.76$ , the shear-thinning effect is observed. Such low value of  $n$  may suggest the large degree of association and entanglement of PAM molecules in solution. The rise of temperature by 20 K does not influence this behavior very much ( $n$  increases from 0.76 to 0.79). In the range of  $\dot{\gamma} > 800 \text{ s}^{-1}$  the parameter  $n$  is equal to 1.20, indicating the shear-thickening behavior. The rise of temperature by 20 K causes pronounced increase of the  $n$  value in the region of shear-thickening (up to  $n = 1.80$ ). Such behavior may be caused by an increase in the number of temporary network or entanglements of the unfolded macromolecules with the increase of temperature. In the case of HPAM (1.5), in the range of lower shear rates ( $19 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 500$ ) the pronounced shear-



**Figure 4** Master curve  $\log \eta/a_T$  versus  $\log \dot{\gamma}$  of PAM ( $c = 1\%$ ) in aqueous/NaCl ( $c = 1\%$ ) solution, at various temperatures: + 298 K;  $\square$ , 308 K;  $\triangle$ , 318 K. Vertical shifting by  $a_T = \eta_T/\eta_{T_o}$ ,  $T_o = 298$  K (reference temperature).

thinning effect is observed ( $n = 0.70$ ). For the range of higher shear rates the parameter  $n$  shows much higher value ( $n = 1.62$ ) than for the PAM solution. For the HPAM (1.5) solution the parameter  $n$  in the all over range of  $\dot{\gamma}$  does not change with temperature ( $\Delta T = 30$  K). The rise of the polymer concentration from 0.5 to 0.8% causes a reduction of  $n$  both in the region of shear-thinning ( $n = 0.51$  for  $c = 0.8\%$ ) as in the region of shear-thickening ( $n = 1.37$  for  $c = 0.8\%$ ). In the case of HPAM solutions of  $\text{DH} \geq 20\%$ , in the range of  $140 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 1220$ , the parameter  $n$  is higher than 1, which indicates shear-thickening behavior. The highest value of  $n$  is obtained for  $\dot{\gamma} \geq 600 \text{ s}^{-1}$ . The rise of polymer concentration of HPAM ( $\text{DH} \geq 20\%$ ) solution causes the less pronounced shear-thickening effect. The value of the rheological parameter  $n$  for the HPAM(20) solution at  $c = 6\%$ , in the range of  $140 \leq \dot{\gamma} \text{ (s}^{-1}\text{)} \leq 1220$ , amounts to 1.04 (Newtonian flow).

### Influence of temperature

Figure 4 shows the master curves obtained using a typical rheological procedure of vertical shifting of the viscosity curves measured at different temperatures. Scaling factor  $a_T$  was determined from viscosity data at constant shear rate  $\dot{\gamma} = 400 \text{ s}^{-1}$ . The rise of the temperature from 298 to 318 K does not induce the pronounced change in the viscosity curves. In the investigated range of shear rates, the apparent viscosity does not change rapidly with the temperature. The constant value of  $\dot{\gamma}_c$  is observed in the range of 298–318 K.

Generally, the magnitude of energy of activation  $E_a$  determines the sensitivity of solutions towards temperature and reflects the influence of the temperature on the intermolecular interaction of the macromolecules in the solvent.<sup>15</sup> The values of activation energy of viscous flow,  $E_{av}$ , were calculated using eq. (2) and are tabulated in Table III for PAM and HPAM solutions, at different shear rates. In the case of the

**TABLE III**  
**Activation Energy of Viscous Flow ( $E_a$ ) of PAM and HPAM Samples**

Polymer	$\dot{\gamma}$ ( $\text{s}^{-1}$ )	$E_a$ (kJ/mol) [eq. (2)]	$R^2$
PAM	250	12.5	0.999
	550	11.1	0.994
	1040	11.8	0.998
HPAM (1.5)	250	28.9	0.973
	550	20.2	0.999
	1040	11.5	0.992
HPAM (20)	250	27.2	0.955
	550	12.4	0.992
	1040	11.4	0.968
HPAM (80)	250	30.2	0.945
	890	9.0	0.986
	1130	11.4	0.998

The polymer concentration and solvent are the same as in Figure 1.

HPAM solutions, the pronounced decrease of  $E_a$  with an increase of shear rate (particularly from 250 to 550  $\text{s}^{-1}$ ) is seen. The highest  $E_a$  value is obtained for the shear-thinning region, when the change of density of entanglements occurs. The value of the  $E_a$  for PAM is practically stable in the shear-thinning and thickening region. For the HPAM solutions, the value of  $E_a$  is practically constant in the shear-thickening region. The value of  $E_a$  amounts to  $\sim 11.5$  kJ/mol, both for the PAM and HPAM solutions. Summarizing, the observed calculated values of the activation energy for the PAM and HPAM solutions mainly depend on the shear rate and on the degree of hydrolysis, in the range of 298–318 K.

#### Influence of aging on apparent shear viscosity $\eta_a$ of PAM and HPAM solutions

The measurements of the effect of aging, in the period of 2 weeks, showed, for 1% PAM solution, that the fall in apparent viscosity was relatively low (3%) in the shear-thickening region ( $\dot{\gamma} > \dot{\gamma}_c = 1040 \text{ s}^{-1}$ ). However after 14 days, the rise of apparent viscosity ( $\sim 12\%$ ) is observed for the shear-thinning region. The effect of aging of PAM solution may be attributed to the association of macromolecules through hydrogen bonds between the amide groups of PAM, which are broken at higher values of  $\dot{\gamma}$ .<sup>16</sup>

In the case of the HPAM solutions, the storage time does not influence the apparent viscosity, practically. One may assume that the apparent viscosity of these solutions is stable (at least during 14 days).

#### Time dependent viscosity

The time dependent apparent viscosity at a constant shear rate above the value of  $\dot{\gamma}_c$  is another important characteristic of the shear-thickening behavior.<sup>1,9</sup> The

studies of the time-dependent apparent viscosity for PAM and HPAM solutions at constant, imposed shear rates 550 and 1040  $\text{s}^{-1}$ , at 298 K, were carried out. The complete time of experiment was equal to 1000 s. In the case of HPAM solutions, the constant and uniform value of viscosity is observed in the time of experiment (1000 s). In PAM solution, the apparent viscosity shows significant fluctuations during the measurement time (especially at 1040  $\text{s}^{-1}$ ) with a tendency to permanent decrease. Such behavior is due to the nature of PAM solution. Fluctuation in viscosity may be caused by the aggregated supramolecular structure existing in solution, which is destroyed at constant imposed shear rate.

## CONCLUSIONS

For the first time the influence of PAM hydrolysis degree (DH in the range of 0–80%) on the rheological properties of PAM solutions has been investigated.

The obtained results confirmed that PAM and HPAM solutions behave as non-Newtonian fluids, which before the critical value of shear rate  $\dot{\gamma}_c$  show shear-thinning behavior. The shear-thickening behavior is observed when the shear rate is above the  $\dot{\gamma}_c$  value. The flow properties of PAM solutions depend on the polymer concentration.

In the case of HPAM solutions, the increase of the PAM hydrolysis degree causes the decrease in the area of shear-thinning behavior and the increase in the area of shear-thickening behavior. The shear-thickening behavior is observed at lower value of  $\dot{\gamma}$  with the increase of the degree of hydrolysis, and with the decrease of polymer concentration. The comparison with the results of other investigators<sup>1,9–11</sup> allow to conclude that the decrease of HPAM molecular weight also increases the shear-thickening area of HPAM solutions in the range of  $0 < \dot{\gamma} (\text{s}^{-1}) < 1200$ . For some peculiar case (HPAM (80), Fig. 1) the effects of orientation and disentanglement may be compensated with the effects of deformation and association and as a result the HPAM solution shows rheological properties close to the Newtonian behavior.

The rheological properties of the polymer solutions were evaluated by fitting the data to a power law model. The power law of the Ostwald de Waele model is a suitable fit for the experimental data of all investigated solutions ( $R^2 > 0.99$ ). The rheological  $n$  parameter depends on the degree of hydrolysis ( $n < 1$  for shear-thinning and  $n > 1$  for shear-thickening), on polymer concentration, and to a lesser extent on temperature.

The effect of aging on the apparent viscosity is observed only for the PAM solutions. The fluctuation of apparent viscosity at imposed shear rate occurs also in the PAM solutions. Such behavior is believed to be

due to structure breakdown under constant imposed shear rate.

Interesting results are related to the activation energy of viscous flow of PAM and HPAM solutions, which is found not to depend on the degree of hydrolysis and molecular weight in the shear-thickening region, in the range of 298–318 K.

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