

Effects of polyacrylamide hydrolysis on molecular characterization

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ABSTRACT

To increase the flocculating ability of polyacrylamide, partially hydrolyzed, for example, up to 30%, anionic derivatives were obtained, which can be highly effective, but it was found that hydrolysis at a higher level leads to the formation of gel structures of polyacrylamide. As a result, anionic polyacrylamide samples aPAA (18%) and aPAA (30%) were prepared, and basic studies were conducted on the principle of comparative comparison of the following three samples. Measurements were carried out on the principle of recording the flow times (t_i) of diluted solutions from the viscometer capillary by adding solvent in discrete amounts from $C = 0.1$ g/dl to $C = 0.02$ g/dl at 25 °C. It was found that diluted solutions in the range of concentration $0 < C < 0.2$ g/dl, then moderately concentrated in the range $0.2 < C < 1.5$ g/dl, and highly concentrated solutions in the range $C > 1.5$ g/dl. From the rheograms, the straight line of diluted solutions and the curves of medium concentration solutions were tested, and the "crossover" concentrations C^* were determined from their intersection points: PAA - $C^* = 0,50$ g/dl; aPAA (18 %) - $C^* = 0,45$ g/dl; aPAA (30 %) - $C^* = 0,40$ g/dl.

Keywords:

Hydrolyzed polyacrylamide, flocculation, anionic polyacrylamide, macromolecular chains, relative viscosity, conformational changes.

Introduction: Polyacrylamide interacts with small particles in solutions and mixtures, surrounds them, covers their surface, and collects them as a separate phase, i.e., forms flocs, largely depends on a number of parameters, such as the polymer's molecular mass, flexibility and mobility to conformational change, ionogenic nature, and the tendency to interact with flocculating particles. [1]. To increase the flocculating ability of polyacrylamide, if it is partially hydrolyzed, for example, up to 30%, it can be highly effective if

an anionic derivative is obtained, but hydrolysis at a higher level leads to the formation of gel-structures of polyacrylamide. Considering that particle flocculation takes place over time under certain thermodynamic conditions, it is certain that this process will continue for a long time if there are no external influences. To accelerate this, it is important to transfer the macromolecules from a cellular state to a spread state, making it possible for them to be surrounded by particles. Such favorable conditions can be created in the flow, for

example, when the molecules move to a spread and oriented ordered state under the influence of symmetric penetrating force lines along the central axis of the longitudinal flow. For systematic research, partial alkaline hydrolysis of selected polyacrylamide, determination of molecular mass and conformational characteristics, preparation of microparticles of sulfur and mixing with polyacrylamide in water to form a suspension, study of structural and phase change characteristics of the suspension in different modes of "sedimented" and "free" longitudinal flows and it is necessary to determine the possibility and conditions of formation of flocs in laminar and turbulent flows. Structural and phase changes in longitudinal flow can be effective in a short capillary viscometer [2].

Objects and methods/ A sample of polyacrylamide (PAA-S) was partially hydrolyzed in sodium hydroxide medium (NaOH) to obtain an anionic derivative, i.e., some monomer groups have a carboxylate group, which ensures high flocculation of microparticles in a sulfur suspension. For this, 2.5 ml of 5 M NaOH aqueous solution was added to 50 ml aqueous solution of polyacrylamide with a concentration of $C = 1$ g/dl, alkaline hydrolysis was carried out at 50 °C for 1 hour and 2 hours, and 2 samples were taken. The obtained samples were compared with water using 0.1 M HCl and 0.05 M NaOH titrants in the potentiometric titration method, and it was determined that their levels of hydrolysis were $HD = 18\%$ and $HD = 30\%$. As a result, anionic

polyacrylamide samples aPAA (18%) and aPAA (30%) were prepared, and basic studies were conducted on the principle of comparative comparison of the following three samples [3]:

- 1) PAA- nonionic polyacrylamide .
- 2) aPAA (18 %) - anionic polyacrylamide ($HD = 18\%$)
- 3) aPAA (30 %) - anionic polyacrylamide ($HD = 30\%$)

To determine the molecular masses of these samples, an Ubbelode viscometer was used, with a time for the solvent water to flow from the capillary of the working organ to = 80 s. Samples for this $C = 0.1$ g/dl solutions were prepared. Distilled water was used as the solvent for nonionic PAA and a 0.2% NaCl+water binary solvent was used to ensure that the ionic α PAA (18%) and α PAA (30%) samples did not exhibit concentration anomaly effects.[4]

Results and its discussion. Measurements were carried out on the principle of recording the flow times (t_i) of diluted solutions from the viscometer capillary by adding solvent in discrete amounts from $C = 0.1$ g/dl to $C = 0.02$ g/dl at 25 °C.

Relative ($\eta_{nis} = t_i/t_o$), specific ($\eta_{sol} = \eta_{nis} - 1$) and reported η_{sol} / C changes depending on concentration (C) were determined and Huggins $\eta_{sol} / C = [\eta] + k[\eta]^2 C$ according to the formula, graphs of η_{sol} / C binding to C were constructed and they are presented in Figure 1.[4]

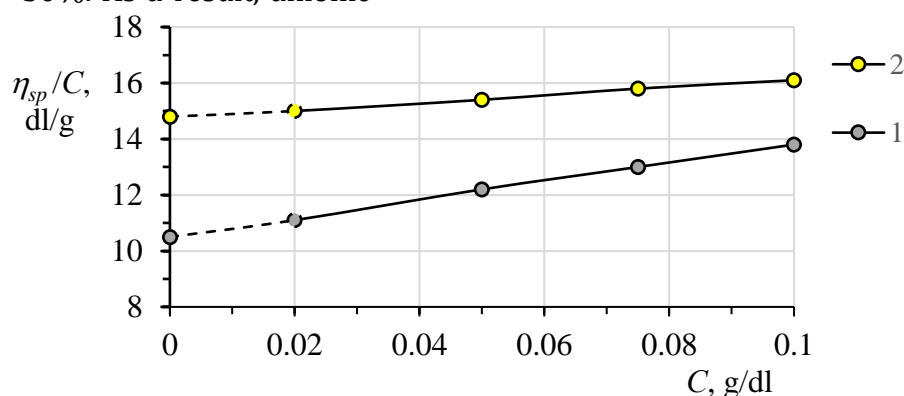


Fig. 1. Dependence of reduced viscosity η_{sol} / C on concentration (C) for PAA solutions in water (1) and HPAA in 0.2% NaCl + water (2) at 25 °C.

If the graph is extrapolated to $C \rightarrow 0$, the condition $k[\eta]^2 C = 0$ and $[\eta]_{sol}/C = [\eta]$ are fulfilled in the Huggins formula. Based on this, the characteristic viscosities $[\eta]$ of the samples

were determined from the graphs, and the molecular masses (M), the distance between the ends of the macromolecular chains $\langle h^2 \rangle$, and the radius of the elementary links ($\langle R \rangle$) were calculated based on it (table 1).

Table 3.1.1. Molecular mass characterization of polyacrylamide samples

Namuna	$[\eta]$, dl/g	$K \times 10^{-5}$, dl/g	a	$M \times 10^6$	$\langle h^2 \rangle$, nm	R , nm
PAA	10,5	6,31	0,80	3,361	372	152
aPAA (18 %)	14,8	6,15	0,82	3,675	511	208
aPAA (30 %)	17,5	6,45	0,83	3.754	590	240

A comparative comparison of the results in the table showed that due to partial alkaline hydrolysis of the samples, that is, HD reaches 18% and 30%, as a result of increasing the amount of carboxylate group in the elementary units of the monomer, their molecular mass increases by 1.09 and 1.12 times. Also, the average distance between the ends of the macromolecular chains showed that HD increased by 1.37 times for the 18% sample and 1.57 times for the 30% sample. Such significant differences were also observed in the radii of the elementary links. Such changes indicate that active ionogenic groups have appeared in the

hydrolyzed samples of polyacrylamide, and a great opportunity has been created for their molecular chains to be in a partially extended conformational state in solutions and to more effectively implement their flocculation properties.[5]

The mobility of the samples to make conformational changes and the manifestation of flocculation properties largely depend on their concentration in the solutions. To analyze this, the relative viscosity ($[\eta]_{rel}$) was measured in a wide range of concentrations, and based on it, the connection graphs presented in Figure.2. were created.

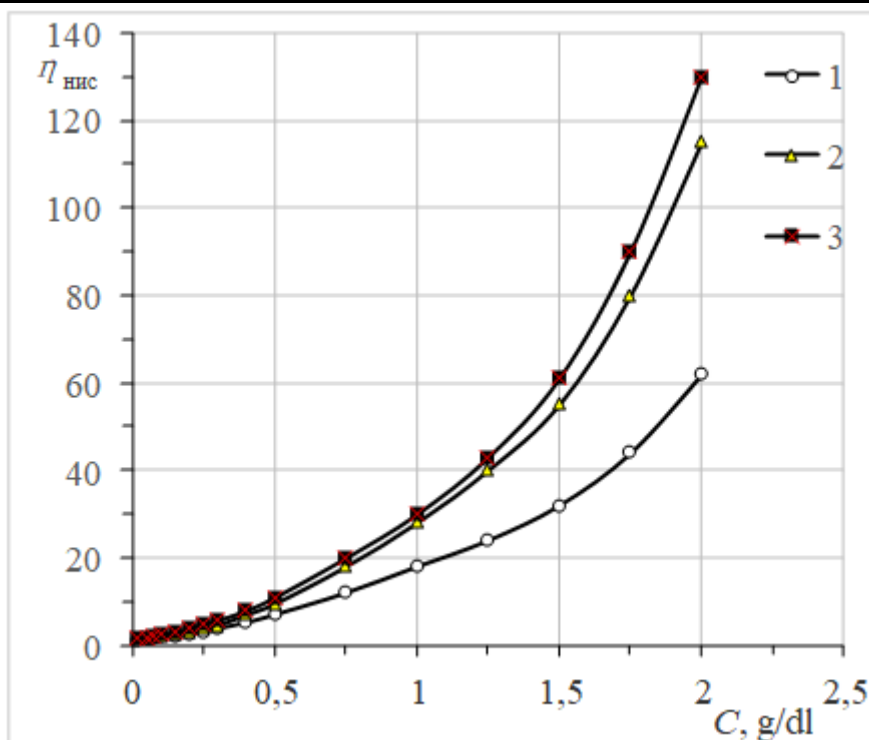


Fig. 2. Dependence of relative viscosity (η_{nis}) of polyacrylamide samples on concentration (C): 1- PAA; 2- aPAA (18%); 3- aPAA (30 %)

In this connection graph, dilute solutions in the range of concentration $0 < C < 0.2$ g/dl $C/[\eta] < 1$, i.e., the area where macromolecules do not interact with each other, in which polymer chains can make free conformational changes and perform flocculation effects at a high level is convenient [35].

In the next range of $0.2 < C < 1.5$ g/dl, a deviation from the straight line connection of the graph, that is, a fluctuation effect, was observed, and this was manifested in the form of a monotonous increase of the relative viscosity. The reason for this is the limitation of the possibility of free movement due to the mutual approach and friction of macromolecules with an increase in concentration. Such a situation is characteristic of moderately concentrated, i.e., semi-diluted solutions, and it was determined from the graphs that they appear in the range of $1.0 < C/[\eta] < 10$.

In the same way, in the next $C > 1.5$ g/dl area, there are high-concentrated solutions, where the increase in concentration results in the deformational densification of macromolecules, their penetration into each other's volume, and effects typical of the

formation of fluctuating nets. For this field, the condition $C/[\eta] > 10$ is valid.

It was observed that all samples lose fluidity in the concentration range of $C > 2.0$ g/dl, i.e. they form clear fluctuation nets and pass to the state of physical gel-structure.

From the graphs, the "crossover" concentrations C^* were determined from the straight line of dilute solutions and the curves of medium concentration solutions from their intersections:

- PAA — $C^* = 0,50$ g/dl;
- aPAA (18 %) — $C^* = 0,45$ g/dl;
- aPAA (30 %) — $C^* = 0,40$ g/dl.
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In general, polyacrylamide samples are thermodynamically favorable for macromolecules to exist in solutions in a "bumpy" conformation, where they may not interact, collide, and stick together in a concentration-dependent manner. Such concentration states are conditionally divided into two areas, that is, "dilute solutions" where macromolecules do not stick to each other, and "semi-dilute (or semi-concentrated) and concentrated solutions" that stick to each other. In dilute solutions, macromolecules are

separated from each other at a much greater distance than their specific sizes, they do not interact with each other, they are isolated. It is very favorable for free conformational changes and flocculation.

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