Rheological Behaviour of Solutions of Polyacrylamide Modified by Mannich Reaction

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Solutions of polyacrylamide modified by Mannich reaction and quaternized have various applications: purification of waste and potable water, decrease of friction coefficient in fluids transport, textile industry, food industry, paper industry etc. These solutions show instability characterized by the variation of viscosity in time, fact that influence their properties. This paperwork studies the rheological behaviour of the solutions of polyacrylamide modified by Mannich reaction with different degrees of transformation of amidic groups (7, 15, 25, 35 and 43 mole/mole %). These solutions are very active in purification of potable and waste water.

Keywords: polyacrylamide, cationic polymer, Mannich reaction, viscosity

Polyacrylamide (PAA) and its derivatives as aqueous solutions are used in various domains: purification of waste water, purification of potable water, decrease of friction in fluids transport, textile industry, food industry, cellulose processing, cosmetics, medicine etc. [1-6].

The viscosity of the solutions of polyacrylamide and its derivatives decreases over time, fact that lead to the decrease of the flocculation capacity and a decrease of the frictions in fluids transport [7, 8]. Considering the applications of aqueous solutions of polyacrylamide and its derivatives, literature reports research studies on this subject and propose several mechanisms [7, 9] for PAA or hydrolyzed PAA. No studies are reported on solutions of polyacrylamide modified by Mannich reaction with different degrees of transformation of the amidic groups. These polymers proved to be very efficient in the purification of potable water, obtained from rivers with high content of inorganic particles [6].

This paperwork presents a rheological study of polyacrylamide and polyacrylamide modified by Mannich reaction with different degrees of transformation. The results of the rheological study are then correlated with the flocculation capacity of the polymer.

Experimental part

Polyacrylamide (PAA) was obtained by inverse polymerization of acrylamide with persulphate-metabisulphite initiating system [10]. A linear and high molecular weight polymer (M>10^6 g/mole) is obtained by this method. These characteristics are very useful in the flocculation process. After methanol extraction, polyacrylamide was dried at 40°C under vacuum. The average molecular weight \( M_v \) of the polymer was viscosimetrically determined in aqueous solution of 1N sodium nitrate at 30±1°C from the following equation:

\[
[\eta] = K \cdot \bar{M}^a, \quad (1)
\]

where \([\eta]\) = intrinsic viscosity and the two constants “K” and “a” known (K=1.34·10^-5 mL/g and a=0.54) [11].

Two samples P₁ with \( M_v =3.6x10^6 \) g/mole and P₂ with \( M_v =12.4x10^6 \) g/mole were used in this experiment.

The modification of polyacrylamide by Mannich reaction was performed in solution in the presence of paraformaldehyde, (CH₂O)n, and dimethyl amine, (CH₃)₂NH at 60°C for 6 h and the final pH of 4.5 was achieved with 0.1N hydrochloric acid solution. The polymer was recovered by lyophilization. The ratio of the total components of the reaction mixture and the final chemical composition of the Mannich modified PAA (PAAM) (determined by elemental analysis) are presented in table 1.

PAAM solutions of 0.08 g/dL concentration were analysed with Ubbelohde-type viscosimeter placed in a AVS 350 device for automatic time measuring.

Reduced viscosity (\( \eta \_r \_sp/c \)) was computed with the following equation (1):

\[
\eta \_r \_sp/c = \eta \_sp/c \_solution - \eta \_sp/c \_reference = \eta \_solution - \eta \_reference \/ c \_solution - c \_reference, \quad (2)
\]

where t=flowing time (s), c=solution concentration (g/dL)

Results and discussions

Polymers P₁ and P₂ were modified by Mannich reaction leading to polymers with different degrees of transformation of the amidic groups between 6 and 43%. These values were obtained from elemental analysis data.

The reduced viscosity of the P₁ and P₂ polymer solutions, respectively of the polymers solutions modified by Mannich reaction (P₁1-P₁4 and P₂1-P₂4) depends on time, thus proving the instability of the solutions. This will alter the properties of the solutions, especially the flocculation capacity. The variation of the reduced viscosity with time is shown in figures 1 and 2.

Figures 1 and 2 show an increase of the reduced viscosity at the beginning of the study reaching a maximum after four days, then it continuously decreases.

The presence of a maximum for PAA and PAAH was studied and explained in [7]. The increase of the chain flexibility by dissolution leads to the increase of the chain mobility and the amidic groups favour the formation of

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intramolecular bonds. This phenomenon is responsible also for the increase of the solution viscosity. In the same time, water molecules interpose between the amidic groups, which have formed intramolecular hydrogen bonds and the chain becomes more flexible and the viscosity decreases. At the beginning of the study (1-4 days) the first phenomenon prevails although the two phenomena overlap and the final effect is the increase of the viscosity (fig. 3).

Kulicke mechanism could also be applied for PAAM and thus we can explain the presence of the maximum for the reduced viscosity in the figures 1 and 2.

The decrease of the viscosity of PAAM solutions is the same for samples with very different molecular weights: \( P_1 - M = 3.6 \times 10^6 \) and \( P_2 - M = 12.4 \times 10^6 \). The difference between the initial and final values of the viscosity for \( P_1 \) and \( P_2 \) are similar (\( \Delta \eta_{sp}/c = 1 \text{ dL/g} \)).

In the case of PAAAM with different degrees of transformation of the amidic groups we can notice a slight increase of the viscosity difference for the sample with higher molecular weight polymer.

The sedimentation rate depends on the dimensions of the macromolecular coil, expressed by the solution viscosity (viscosity increases with the increase of the macromolecular coil). Figure 4 shows the dependence of the sedimentation rate (rate of the formation of the clear phase in 3% aqueous solution of clay, expressed in mL/s) using a solution of 0.1% PAAM immediately after preparation and after 20 days of conservation. The flocculation capacity, here expressed by sedimentation rate decreases for the low viscosity solution (20 days conservation).

Several additives were used to stabilize PAA solutions: ethylene glycol, urea and isopropanol [7, 8]. These additives do not block the appearance of a maximum within the curve \( \eta_{sp}/c \) versus time, but they maintain the initial value of the viscosity even after 20 days. We suppose these

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \bar{M} \times 10^{-6} ) g/mole</th>
<th>( [\text{CH}_2\text{O}] = [\text{DMAD}] ) mole</th>
<th>( [-\text{CONH}_2] ) mole</th>
<th>( \text{Transf. groups} [-\text{CONH}_2] ) mole</th>
<th>( \text{Total groups} [-\text{CONH}_2] ) mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_1 )</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( P_{11} )</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>( P_{12} )</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>( P_{13} )</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>( P_{14} )</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>( P_2 )</td>
<td>12.4</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( P_{21} )</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( P_{22} )</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>( P_{23} )</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>( P_{24} )</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>40</td>
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additives form hydrogen bonds with the amidic groups, which cannot be replaced by water-amidic functions bonds.

Furthermore, glycerol was proposed for PAAM used in water purification. Glycerine proved to be very efficient in maintaining the viscosity of PAAM solutions over time.

Figure 5 shows the variation of $\eta_{sp}/c$ versus time for a 0.08% PAAM solution ($P_{12}$) with and without glycerol as additive (2% versus the total solutions).

Fig.3. Increase of chain flexibility by interposing of the water molecules between the amidic groups with intramolecular hydrogen bonds (Kulicke mechanism)

Fig.4. Sedimentation rate (mL/s) for a 3% clay suspension with 0.1% PAAM (sample $P_1$) with different Mannich degrees of transformation ($P_{13}$) used immediately after preparation; $P_{13}$ PAAM solutions ($P_{11}$) used after 20 days of conservation

Fig.5. Variation of the reduced viscosity with time for PAAM solution with and without glycerol

Conclusions
Solutions of polyacrylamide modified by Mannich reaction are efficient in flocculation of aqueous suspensions.

These solutions are instable in time, fact that determines the decrease of the viscosity and of the sedimentation rate.

The decrease of viscosity in time is slightly influenced by the value of the molecular weight or by the value of the Mannich degree of transformation.

The presence of glycerol as additive is very efficient in stabilizing the viscosity of PAAM solutions in time.

References
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