Activation parameters of viscous flow of guar gum and its cross-linked system

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Abstract. The structure of a cross-linked form of a concentrated solution of guar gum was studied using IR spectroscopy. The processes of viscous flow of concentrated solutions of guar gum and its cross-linked system have been studied. It is shown that this system is a non-Newtonian fluid with a thixotropic type of viscous flow anomaly, which is also determined by the nature of the complexing agent. The influence of temperature on viscous flow processes, as well as the structure of aqueous systems of guar gum and its cross-linked form, were studied based on the average statistical sizes of kinetic units, which makes it possible to estimate the mobility of structural elements and their sizes for concentrated systems. The activation parameters of the viscous flow of aqueous systems of guar gum and its cross-linked system were studied. Calculations of thermodynamic parameters were carried out free energy, heat of activation of viscous flow, characterizing the strength of structures, and entropy of activation of viscous flow, characterizing the ordering of structures. At high shear stresses, for the guar gum solution system, the processes of ordering and orientation prevail during flow, and for the guar gum - pentaerythritol borate system, the processes of structure destruction and disordering prevail.

1 Introduction

Currently, in the field of bioorganic chemistry, special attention is paid to the production of polysaccharide gels by modifying polysaccharides, the specific molecular structure and features of the supramolecular structure of which make it possible to obtain materials with new properties for use in tissue engineering and the creation of soft dosage forms [1-4]. To regulate the physical and mechanical properties of polymer materials, directed structuring of polymers is used, which is carried out by changing the concentration of the polymer in solution, using modifying additives (structuring agents, co-solvents, plasticizers) or new functional groups that have one or another affinity for the polymer and regulate the interaction polymer-solvent [5-7].

In this aspect, the most interesting and poorly studied is the natural polysaccharide - guar gum (GG) and its complex with boron compounds and polyhydric alcohol - pentaerythritol

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The structure of GG macromolecules determines their high lyophilicity and the ability of this polymer to form highly viscous gels.

From this point of view, GG structures weakly cross-linked through complexes are of greatest interest, since solutions of such systems are capable of forming a gel in a stationary state, and when it is mechanically destroyed under deformation conditions, such systems are capable of irreversible deformations (i.e., flow). In this case, it is possible to evaluate the viscous rheological characteristics, shear stresses that characterize the mechanical strength of the gel, and above which the systems exhibit irreversible deformation properties.

The purpose of the work is to study the structuring process, rheological properties and thermodynamic parameters of concentrated aqueous solutions of guar gum and its cross-linked form.

2 Methods

Objects of research: 1. Guar gum is a polysaccharide obtained by extraction from ground endosperm of the seed plant Cyamopsis tetragonolobus (India), CAS 9000-30-0, Mₘ=1.26·10⁵ Da.

2. Crosslinking agent: borate:pentaerythritol molar ratio 0.1:0.01.

3. Pentaerythritol (PE) – 2.2-bis-(hydroxymethyl)-1.3-propanediol, polyhydric alcohol, chemically pure grade, manufactured by Metafrax OJSC (Gubakha, Russia), CAS 77-15-5.


Studies of the rheological properties of the GG system (1 wt.%) and its cross-linked form were carried out on a rotational viscometer "Reotest-2" with a working unit of coaxial cylinders in the range of shear stresses τ (1.6 - 3·10³) Pa and shear rates D (0.2 – 1.3·10³) s⁻¹ at temperatures 25, 40, 55, 70 °C. Based on the data obtained, the values of the thermodynamic parameters of the systems were calculated - enthalpy ΔHₜ, entropy TΔSₜ and free energy of activation of viscous flow ΔGₜ[8,9].

The temperature dependence of the viscosity of the samples under study in the temperature range 25-70°C is described by the Arrhenius-Frenkel equation: η = A*eΔE/RT, where ΔΕ is the activation energy of the viscous flow [10,11], R is the gas constant.

3 Results and discussion

Guar gum (GG) is a polysaccharide, the main polyglycosidic chain of which consists of mannose residues connected by β-1,4 bonds and galactose residues are attached to some mannose residues via α-1,6 bonds, with one galactose unit per two mannose units [12].

The presence of OH groups in the cis arrangement at the 2nd and 3rd carbon atoms, located on one side of the plane of the carbon ring [13] in GG, makes it possible to obtain cross-linked systems on its basis by forming complexes with borate ions.

When guar gum is cross-linked with boron ions, cloudy, brittle jellies are obtained, which undergo syneresis over time. The introduction of more voluminous spatial complexing agents into guar solutions leads to the formation of an additional fluctuation network with an increased entanglement density, which leads to a significant change in the rheological properties.

It is known that triols containing the β,β-triol group significantly increase the electrical conductivity of boric acid. Based on this, it was concluded that tetraborates are capable of forming anionic complexes with these triols in which boron is four-coordinated and the ligand is tridentate [14,15]. Pentaerythritol (2,2-dimethylolpropanediol) also contains a β,β-triol group, and therefore was chosen as a complexing agent with boron ions.

In order to structure guar gum and obtain a stable, strong gel, a pentaerythritol borate complex was synthesized. The synthesis was carried out in a slightly alkaline (pH=8-9)
environment at a temperature of 80°C and a tetraborate:pentaerythritol molar ratio of 0.1:0.01. As a result, a complex was obtained, the composition of which varies depending on the ratio of components and reaction conditions [16].

When the ratio of pentaerythritol:borate ions is 1:2, i.e. for one molecule of pentaerythritol there are two molecules of borate ion, the complexation reaction proceeds according to the following scheme, and the complex has the following structure:

\[
\text{HOCH}_2\text{C-CH}_2\text{OH} + \text{Na}_2\text{B}_4\text{O}_7 \times 10 \text{H}_2\text{O} \rightarrow \left[\begin{array}{c}
\text{CH}_2\text{OH} \\
\text{HOCH}_2
\end{array}\right] \text{Na}_2\text{B}_4\text{O}_7 \times 10 \text{H}_2\text{O}
\]

The resulting complex was used in the cross-linking reaction of guar gum. The crosslinking reaction was carried out at room temperature and slow stirring, at a molar ratio of guar gum and complex of 1:0.3. In this case, an instant structuring of the guar gum system occurs, and it passes from a fluid state to a non-fluid state, i.e. the viscosity of the system increases and a structured system is obtained - a cross-linked guar gum gel.

It can be assumed that structuring proceeds according to the following scheme:

Features of the mechanical behavior of the structuring system, depending on the nature of the complexing agent and without it at different temperatures, are described by the dependences \( \tau_{cr} = f(T) \) shown in Figure 1.
Rheological studies of changes in the strength $\tau_{cr}$ of the gel structure of 1% aqueous solutions of GG and its structured system under conditions of temperature changes from 25 to 70°C have shown that the so-called bridge bonds formed by the cross-linking agent between polysaccharide macromolecules lead to the formation (at 25°C) of a durable gel $\tau_{cr} = 36.3$ Pa, for GG $\tau_{cr} = 11.0$ Pa. An increase in temperature leads to a significant decrease in strength characteristics for all systems under study [17].

For the solutions of GG and its cross-linked system studied in this work, using a rotational viscometer (first with increasing - a continuous line, then with decreasing rotation - a dashed line) rheograms were obtained in the form of dependences of effective viscosities $\tau \log \eta = f (\log \tau)$, showing their obvious non-Newtonian thixotropic flow character (Fig. 2 (a, b)).

For solutions of guar gum (Fig. 2a), the beginning of intense destruction of the structure at different temperatures, estimated from the obtained rheogram, is shifted to the region of lower shear stresses compared to the structured system GG-pentaerythritol borate (Fig. 2b), which is apparently explained by the formation for GG, a weaker and less uniform network of intermolecular contacts in the associates of the polysaccharide under study than in the cross-linked system. From Fig. 2 (a, b) it is clear that for the studied systems, an increase in
temperature leads to a natural decrease in viscosity parameters and a shift of critical shear stresses to the region of lower values.

The values of the apparent activation energy of viscous flow $\Delta E$ (hereinafter $\Delta E_{\text{app}}$), which is a measure of the intensity of intermolecular interaction of macromolecules in solutions, and, in other words, an indirect characteristic of the strength of the structure of polymer fluid systems in solutions [18], are given below: for GG – $\Delta E_{\text{app}} = 31.02 \text{ kJ/mol}$; GG-pentaerythritol borate - $\Delta E_{\text{app}} = 49.78 \text{ kJ/mol}$. An aqueous solution of GG is characterized by the lowest $\Delta E_{\text{app}}$ values, and, consequently, the lowest strength of the solution structure. The GG-pentaerythritol borate system is characterized by the highest value of $\Delta E_{\text{app}}$, which is explained by the formation of strong bridge bonds, which are also partially preserved under viscous flow conditions.

Based on the results of rheological studies, the values of “viscosity volumes” $V^*$ or the average statistical sizes of kinetic units were estimated, which make it possible to estimate the mobility of structural elements and their sizes for a solution of guar gum and its cross-linked system (Table 1).

Table 1. Change in viscosity volume $V^*$ from temperature and shear stress ($\tau$) for systems: guar gum (1), GG – pentaerythritol borate (3)

<table>
<thead>
<tr>
<th>$\tau$, Pa</th>
<th>T, K</th>
<th>$V^*$·10$^{-23}$, m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1% solution GG</td>
</tr>
<tr>
<td>10</td>
<td>298</td>
<td>791.5</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>827.2</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>855.7</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>902.6</td>
</tr>
<tr>
<td>20</td>
<td>298</td>
<td>425.1</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>447.4</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>463.0</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>484.6</td>
</tr>
<tr>
<td>30</td>
<td>298</td>
<td>306.8</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>324.2</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>330.2</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>350.7</td>
</tr>
</tbody>
</table>

From Table 1 it can be seen that with increasing temperature there is an increase in the $V^*$ values for solutions of guar gum and the cross-linked system over the entire temperature range from 25 to 70°C, which is explained by the unfolding of macromolecules and the facilitation of intermolecular interactions and rearrangements, as a result of which associates of various types are formed.

For solutions of guar gum, the $V^*$ values are lower compared to its cross-linked system, which has the highest $V^*$ values. This change in $V^*$ values is explained by the influence of the nature and structure of the complexing agent, or more precisely, by the specificity of the formation of bridge bonds between the hydroxyl functional groups of pyranose rings, also determined by the configurational structure of the galactomannan polymer matrix.

Calculations of thermodynamic parameters were carried out: free energy $\Delta G_B$, heat of activation of viscous flow $\Delta H_B$, characterizing the strength of structures, and entropy of activation of viscous flow $T\Delta S_B$, uniquely related to the structure of the polymer and characterizing the ordering of structures [8], which provide additional information about the structure of the systems under study (Table 2).

Table 2. Dependence of thermodynamic parameters ($\Delta G_B$, $\Delta H_B$, $T\Delta S_B$) on temperature in the region of low shear stresses

<table>
<thead>
<tr>
<th>Indicators</th>
<th>System</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of activation of viscous flow $\Delta H_B$, kJ/mol</td>
<td>1% GG</td>
<td>25 25 25</td>
</tr>
<tr>
<td></td>
<td>GG-pentaerythritol borate</td>
<td>62 48 35</td>
</tr>
</tbody>
</table>
The quantities $T \Delta S_B$ and $\Delta H_B$ are functions of temperature. The temperature dependence of these quantities is greater, the more associated the systems are, the greater the energy of intermolecular interaction. As the temperature increases, these bonds are destroyed by thermal motion, therefore $\Delta H_B$ decreases, which is observed for the system under study. From Table 2 it can be seen that for the GG-pentaerythritol borate system, in which structure formation is clearly expressed, the parameters $\Delta H_B$ and $T \Delta S_B$ at ordinary temperatures are very high and decrease with increasing temperature. High values of $\Delta H_B$ for this system are associated with energy consumption for the destruction of the solution structure, and high positive values of $T \Delta S_B$ indicate disordering of the structure during the transition from the initial to the active state. The GG-pentaerythritol borate system is more structured compared to a concentrated GG solution. The values of $T \Delta S_B$ and $\Delta H_B$ for GG solutions are relatively small and do not depend (or weakly depend) on temperature. For viscous flow processes [8], a compensation effect for $T \Delta S_B$ and $\Delta H_B$ is observed, as a result of which the values of $\Delta G_B$ for the polymer complex system of GG are almost independent of temperature. For GG solutions at low shear stresses, with increasing temperature, macromolecules unfold, intermolecular interactions are facilitated, as a result of which associates of a more ordered type are formed. This state of solutions is characterized by higher order ($T \Delta S_B<0$). Therefore, the $T \Delta S_B$ values of GG solution systems become more negative with increasing temperature.

High shear stresses $\tau$ lead to fundamental changes in the initial structure of GG systems and its cross-linked form (Table 3).

### Table 3. Dependence of thermodynamic parameters ($\Delta G_B$, $\Delta H_B$, $T \Delta S_B$) on shear stress $\tau$ at 25°C

<table>
<thead>
<tr>
<th>Indicators</th>
<th>System</th>
<th>Shear stress $\lg \tau$ (τ, Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of activation of viscous flow $\Delta H_B$, kJ/mol</td>
<td>1% GG</td>
<td>30.0 30.0 30.0 30.0</td>
</tr>
<tr>
<td></td>
<td>GG-pentaerythritol borate</td>
<td>- - 60.0 43.3 42.5 41.1</td>
</tr>
<tr>
<td>Entropy of activation of viscous flow $T \Delta S_B$, kJ/mol</td>
<td>1% GG</td>
<td>1.5 0 1.5 2.5 - -</td>
</tr>
<tr>
<td></td>
<td>GG-pentaerythritol borate</td>
<td>- - 25.0 14.0 10.0 8.0</td>
</tr>
<tr>
<td>Free energy $\Delta G_B$, kJ/mol</td>
<td>1% GG</td>
<td>30.0 29.0 28.2 26.0</td>
</tr>
<tr>
<td></td>
<td>GG-pentaerythritol borate</td>
<td>- - 35.9 34.0 32.5 31.0</td>
</tr>
</tbody>
</table>

As can be seen from Table 3, with an increase in $\tau$ to 100 Pa, the values of $T \Delta S_B$ and $\Delta H_B$ sharply decrease. This is explained by the mechanical destruction of associates based on the GG-pentaerythritol borate complex, since they are formed by the complexing agent mainly at the hydroxyl groups of the side galactopyranose groups and do not have short-range order. For GG solutions, with increasing shear stress, a slight increase in the activation entropy $T \Delta S_B$ is observed with almost unchanged activation heats $\Delta H_B$. This indicates some ordering of the macromolecular rigid-chain systems of galactomannan, the macromolecules and associates of which acquire a certain preferential orientation along the flow direction under the action of an applied shear stress. Regardless of whether ordering or disordering processes occur during the flow, shear stress reduces the value of free activation energy $\Delta G_B$, which leads to a decrease in viscosity. For the GG-pentaerythritol borate system, this occurs up to certain values of $\tau$, which manifests itself in a flow with the lowest Newtonian viscosity. When the temperature of the systems increases to 70°C, a sharp and significant increase in
the heat of activation and entropy of activation of viscous flow is observed for GG and its cross-linked form. This effect for the polysaccharide under study - GG and its cross-linked form - is accompanied by pronounced disordered structuring and is caused by an imbalance of dispersed, ionic, dipole, hydrogen and other interactions.

4 Conclusions

1. The processes of viscous flow of concentrated solutions of GG and its cross-linked system were studied. It is shown that these systems are non-Newtonian fluids with a thixotropic type of viscous flow anomaly, which is also determined by the nature of the complexing agent. The influence of temperature on the processes of viscous flow of a structured system is assessed.

2. The structure of concentrated aqueous systems of GG and its cross-linked form was assessed based on the average statistical sizes of kinetic units, which makes it possible to estimate the mobility of structural elements and their sizes.

3. The activation parameters of the viscous flow of aqueous systems of GG and its cross-linked system were studied. The thermodynamic parameters of viscous flow are estimated: free energy, activation heat and activation entropy. It has been shown that structure formation is clearly expressed for the GG-pentaerythritol borate system. At high shear stresses, for the GG solution system during flow, the processes of ordering and orientation prevail, and for the GG-pentaerythritol borate system, the processes of structural destruction and disorder prevail.

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