

# REPUBLIC OF AZERBAIJAN

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## ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

### **THE INFLUENCE OF SOME HYDROPHILIC AND HYDROPHOBIC ADDITIVES ON THE PHYSICO-CHEMICAL PROPERTIES OF AGAROSE HYDROGEL**

Speciality: 2206.01 – Molecular physics

Field of science: Physics

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**BAKU-2024**

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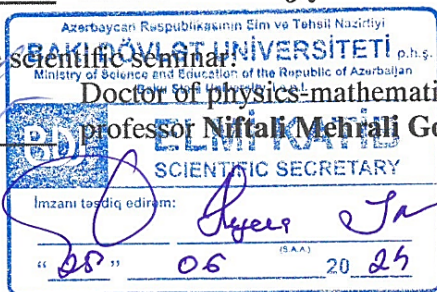
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## GENERAL DESCRIPTION OF THE WORK

**Relevance of the topic and degree of elaboration.** Polymer gels have unique properties not found in other materials: they can hold more than 1000 times their own weight in solvent and can be deformed by more than 10 times. Due to these properties, hydrogels (gels formed in water) have a wide range of applications. Among them, it is widely used in medicine, materials science, biotechnology, food technology, cosmetology, etc. These include organ engineering (replacement of organs such as bone, cartilage, soft contact lenses, muscles and soft tissues with artificial organs that are insensitive to the body), ceramic technology (production of very small parts using 3D printers), pharmacology (storage of drugs, extension of validity and delivery to the target organ), food industry (improving the quality of marmalade, ice cream and many food products and extending their shelf life, creating artificial foods and absorbent materials) etc. can be shown. Recently, great efforts have been made to develop hydrogels as tissue replacement materials for future medical applications and connective strands for regenerative medicine. At the same time, it should be noted that many processes occurring in living organisms occur in heterogeneous biopolymer systems, which can be considered as analogues of gels. All this shows that it is very important to search, purchase, study and recommend gels with known properties according to the specific application. The study of the mechanism of the sol-gel phase transition in polymer gels, the laws of formation of their structure, a number of properties of both solids and liquids (elasticity, its study as a special phase case that contains high elasticity, non-fluidity, propagation of sound waves) is also very important with theoretical point of view.

Considering the above, linking the physical properties of polymer gels with their structure and proving the possibility of targeted control of the properties of gels is of great theoretical and practical interest.

Although many studies have been conducted on the influence of various factors on the physical properties of the agarose gel

studied in this work, we believe that the scientific basis for controlling these properties has not been fully developed. A dissertation can serve to fill this gap, at least partially.

### **Object and subject of research**

The object of the study was powdered agarose obtained from red seaweed produced by the Swiss company CONDA. We took hydrogels obtained from aqueous solutions.

The aqueous solutions of agarose, physical properties of hydrogels formed under the influence of temperature and various organic and inorganic low-molecular compounds (Sodium salt of tartaric, succinic and citric acid, NaCl, KCl, CaCl<sub>2</sub> and isoamyl alcohol) also the investigation of the sol-gel phase transition in these gels was the subject of the presented work.

### **The main goal and objectives of the study:**

As already mentioned, gels, especially hydrogels, have a wide range of applications: medicine, food industry, pharmacology, materials science, etc. The variety of application areas requires the acquisition of gels suitable for these areas. In order to obtain gels with the necessary properties, the main goal of the work is to study the physical and physicochemical properties of gels, the solution-gel phase transition and the influence of various organic and inorganic low-molecular compounds on these properties. .

To achieve this goal, the following issues were resolved:

- Viscosity, intrinsic viscosity, Huggins constant and activation parameters of aqueous solutions of agarose were determined by rheological methods, and the influence of various organic and inorganic low-molecular compounds on these parameters was studied.
- Using a rotational viscometer, the rheological properties of agarose gel and the influence of various organic and inorganic low-molecular compounds on these properties were studied;
- Using the dynamic light scattering method, the dependence of the number and size of particles in an aqueous solution of agarose on the concentration of agarose, as well as the influence of various organic and inorganic low-molecular compounds added to the solution, was established. this dependence has been studied;

- Using UV-Vis spectroscopy, the dependence of gelation and melting temperatures on agarose concentration and the influence of various organic and inorganic low-molecular compounds on this dependence were studied;
- Using the method of low-frequency dielectric spectroscopy, the dependence of the number and size of agarose particles in an aqueous solution on the concentration of agarose, as well as the influence of various organic and inorganic low-molecular compounds added to the solution, was established. this dependence has been studied;
- Using the conductometry method, the nature, concentration, mobility of ions in an aqueous solution of agarose and changes in the magnitude of these quantities caused by various hydrophobic and hydrophilic additives were studied.

**Research methods:**

The research work used methods of rheology, rotational viscometry, UV-visible spectrophotometry, low-frequency dielectric spectroscopy, dynamic light scattering and conductometry.

**Main provisions for the defense:**

1. Determination of the influence of agarose concentration and various additives on the activation parameters of viscous flow in an aqueous solution of agarose;
2. Determination of gelation ( $T_{gel}$ ) and gel melting ( $T_m$ ) temperatures at various agarose concentrations and the evaluation of changes in these temperatures caused by various additives;
3. Research of the hysteresis curves observed on the temperature dependence of optical density and characterizing the thermal strength of the gel.
4. Study of the electrical properties of the gel, as well as the influence of the concentration of agarose and different additives included in the gel on these properties.

**The scientific novelty of the research:**

1. Based on viscometric measurements, various conformational states of the macromolecule in aqueous solutions of agarose were studied. At the same time, the transition temperature of one of

these conformational states to another and the effect of additives on this temperature were studied.

2. Measurements carried out using a rotational viscometer show that increasing the concentration of agarose leads to an increase in the yield stress and the lowest Newtonian viscosity. The addition of salts NaCl, KCl and CaCl<sub>2</sub> in a small amount (0.5 mol%) significantly increases its viscosity. It has been established that these salts have different effects on the magnitude of flow stress. NaCl salt almost does not change the yield strength, CaCl<sub>2</sub> significantly increases it. KCl salt, on the other hand, greatly increases the yield stress.
3. Studies carried out by the light scattering method show that there are two types of particles in the structure of an agarose gel: large particles, the size of which depends on the concentration of agarose, temperature and storage time at a given temperature; small particles, the size of which does not depend on the factors mentioned above. Smaller particle sizes correspond to isolated coils. Large particles are associations that include a large number of coils.
4. As a result of the measurement of the turbidity spectrum of the agarose gel, the thermohysteresis properties observed in it were studied and it was shown that the formation of the gel occurs in a narrower temperature interval than its dissolution (melting). The degree of hysteresis, that is, the difference between the melting and non-gelling temperatures of the gel, increases with the increase in the concentration of agarose.
5. Using the method of low-frequency dielectric spectroscopy, it was shown that a hydrophobic additive weakly changes the dielectric relaxation of an agarose gel, and a hydrophilic additive shifts it to the low frequency region. These properties are associated with changes in the viscosity of the solution.
6. Using the results of measurements conducted using the conductometric method, it was shown that the temperature dependence of electrical conductivity in the agarose-water system exhibits a hysteresis property. The effect of agarose concentration, as well as hydrophobic and hydrophilic additives on the area of

hysteresis (gel strength) was studied. It is shown that additives of a hydrophilic nature strengthen the gel: the temperatures of degelation and melting of the gel shift upwards. On the other hand, the hydrophobic additive weakens the gel, i.e. shifts the temperature of degelation and melting of the gel down.

### **Theoretical and practical significance of the research:**

Agarose, chosen as the object of study, is widely used in various fields of science and industry (food industry, ceramic technology, medicine, biotechnology, etc.). By adding various organic and inorganic compounds to the agarose-water system, it is of great practical importance to obtain gels with the necessary physical properties in the specified areas and specific technological processes. One of the aspects that attracts special attention is that the study of agarose solutions in water in gel-forming and non-gelling concentrations, in the main components of living organisms (blood, cells, tissues, brain matter, etc.) helps to deeply understand the processes and their properties, model them and apply the results obtained in organotechnics (creation of artificial muscles, cartilage, etc.).

### **Approval and application:**

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2. Əmrahova, A.H. “Aqar məhlulunda geləmələgəlmə proseslərinin öyrənilməsi” // Magistrantların və Gənc Tədqiqatçıların “Fizika Və Astronomiya Problemləri” Respublika Elmi Konfransı, – Bakı: Müəllim nəşriyyatı, 22 may, –2014, –s.96.
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4. Məsimov, E.Ə., İmaməliyev, A.R., Əmrahova, A.H. “Aqar məhlulunda geləmələgəlmə proseslərinin spektrofotometrik

- metodla öyrənilməsi” // Gənc Tədqiqatçıların II Beynəlxalq Elmi Konfransı, – Bakı: Qafqaz Universiteti nəşriyyatı, 18- 19 Aprel, – 2014, – s-62.
5. İmaməliyev, A.R., Əmrahova, A.H. “Aqaroza məhlulunda geləmələgəlmə prosesinin işığın dinamik səpilməsi metodu ilə tədqiqi” // Fizikanın Müasir Problemləri VIII Respublika Konfransı, “Opto, nanoelektronika, kondensə olunmuş mühit və yüksək enerjilər fizikası, – Bakı: Bakı Universiteti nəşriyyatı, 25-26 dekabr, – 2015, – s.262 - 263.
  6. Məsimov, E.Ə., İmaməliyev, A.R., Əmrahova, A.H., Prudko, V.V. “Aqarozanın sulu məhlulunda geləmələgəlmə prosesinin spektrofotometrik metodla tədqiqi” // Müasir Təbiət Və İqtisad Elmlərinin Aktual Problemləri Beynəlxalq Elmi Konfransı, – Gəncə: 04-05 may, –2018, –s.182-184.
  7. Asadova, A.H., Masimov, E.A. “The determination of intrinsic viscosity by viscometer”//Academician G.B.Abdullayev Centenary İnternational Conference and School Modern Trends in Condensed Matter Physics , – Bakı: 24-26 sentyabr , –2018, –s.49
  8. Məsimov, E.Ə., Asadova, A.H., Bağırova, S.B., Prudko, V.V. “The temperature dependence of intrinsic viscosity of agarose’s liquid solutions”// İnternational Conference Modern Trends in Physics, – Bakı: Bakı Universiteti nəşriyyatı, 01-03 may, – 2019, – p.133-134.
  9. Масимов, Э.А., Асадова, А.Г., Прудко, В.В., Шахвердиев, Я.Х.“Температурная Зависимость Характеристической вязкости водных растворов агарозы”// XII Всероссийская Школа-Конференция Молодых Ученых Теоретическая И Экспериментальная Химия Жидкофазных Систем, Иваново: 7-11 октября – 2019, – с.74 -75.
  10. Asadova, A.H. “ Hydrophilic additives on the dielectric properties of agarose gel” // Silk Road International Scientific Research Conference, – Baku: December 8-9, –2022, –s.360.
  11. Асадова, А.Г. “Исследование светопропускания водного раствора агарозы” / II Международная Научная Конференция «Современные Тенденции Развития Физики



Полупроводников: Достижения, Проблемы И Перспективы,  
– Ташкент: 27-28 декабрь, – 2022 , – с.368-369.

The results of the dissertation were published in 10 scientific articles and 11 conference proceedings, 2 of which were included in impact factor journals included in the Web of Science database.

**The name of the institution where the dissertation work was completed.**

The dissertation work was carried out at the Department of “Structure of Matter” of the Faculty of Physics of Baku State University.

**Structure, volume and main content of the dissertation work.**

The dissertation consists of an introduction, five chapters, results and the list of 166 used references, 71 figures, 11 tables. The scope of the work consists of 188289 characters.

## CONTENT OF WORK

**In the introduction** the relevance of the topic is substantiated, the purpose of the work, scientific innovations in the work, the main scientific provisions submitted for defense are explained, information is provided about international and domestic conferences at which the results of the research conducted are discussed. The scientific and practical significance of the dissertation was also indicated, and a summary of the chapters was interpreted.

**Chapter I** is a summary and consists of a brief overview of the scientific work which is done on the rheological, spectrophotometric, thermal and electrical properties of agarose hydrogel.

**Chapter II** had been presented technology of preparing agarose gel. In the process of preparing the gel, the agarose powder was first weighed on ADAM PW124 scales (with an accuracy of 0.001), added to it the required amount of bidistilled water and kept for one day for swelling (the globules open and move). (until accidental washing). Then the gel was placed in a mixed water bath at a temperature of 90°C-95°C, in the case of non-forming concentrations (or transparent cases) they were kept for 30-40 min. in

the case of gel-forming concentrations - 1-2 hours before obtaining a homogeneous solution (with frequent stirring and stirring). After preparation, the samples were filtered while hot through a Schott No. 4 filter to ensure sterility. As a result, transparent, colorless, odorless solutions were obtained. The hot solution was poured into the viscometer, spectrophotometer cuvette, etc., which will be used for the experiment. The process was carried out by cooling from the upper temperature (90°C-95°C) to the lower temperature (15°C-20°C) and thus determined the inlet temperature. In order to study the reverse process, the sample is heated for 24 hours, starting from room temperature, until the moment of melting, as a result of which the melting temperature of the gel is determined. When considering the effect of additives, their solution in water was used as a solvent.

In this chapter, the rheological methods which is used in the study of the physical properties of agarose gel, the method of dynamic light scattering, which is considered one of the most accurate methods used to determine the size of particles, conductometry, used to measure electrical conductivity in solutions, spectrophotometric method of measurement of optical density, absorption of incident, light passing through an object, as well as dielectric spectroscopy and information about devices were also given.

**Chapter III** the rheological properties of agarose gel and the effect of temperature and various additives on these properties were studied. The temperature dependences of viscosity, intrinsic viscosity, activation parameters and yield stress were established.

In order to determine the temperature at which the conformational transition “flake-rigid stick” occurs, the temperature dependences of the  $[\eta]$ -characteristic viscosity and the Huggins  $k'$ -constant were studied (in the temperature range 20°C÷70°C). It has been established that the agarose-water system has an upper critical solubility temperature (HYKT), that is, with increasing temperature, the thermodynamic quality of the solvent increases (the avidity of the solvent to the polymer increases, the second virial coefficient ( $A_2$ )). As a result, with increasing temperature, the penetration of the solvent into the polymer bath increases, the flake swells, its volume

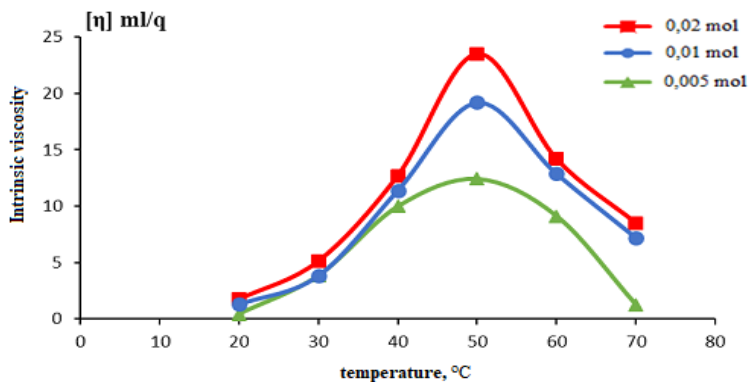
increases, and, as a consequence, this is accompanied by an increase in resistance to hydrodynamic flow or intrinsic viscosity. The Huggins constant characterizes the resistance to solvent penetration into a statistical flake, and its value decreases monotonically with increasing temperature<sup>1</sup>.

The influence of a number of organic acids (citric, tartaric, succinic) on the parameters  $[\eta]$  and  $k'$  of sodium salts was studied (Fig. 1).

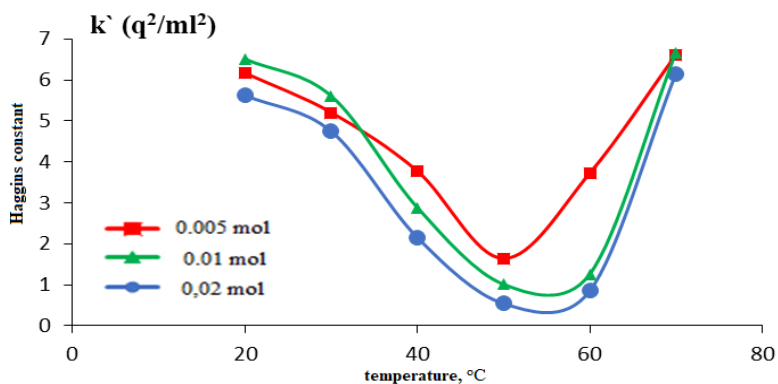
As you can see, these dependencies have a close character. As the temperature increases, the characteristic viscosity first increases, and then decreases after passing a certain maximum. The Huggins constant first decreases, and then increases after passing through a certain minimum. To explain the obtained results, we note that salts falling into an aqueous environment undergo dissociation and a hydrate layer consisting of water molecules is formed around each ion. Along with free water molecules, relatively small sodium ions accumulate in the static flake, which accumulates there, preventing subsequent sodium ions from penetrating into the flake. At this time, the increase in the size of the flake (swelling) weakens and this characteristic leads to a decrease in viscosity. In addition to this effect, it should be taken into account that the ions in the solution form a complex with the hydrophilic functional groups of the agarose macromolecule, enter into hydrogen bonds with the water molecules in the volume and sharply reduce the decay effects. structure of water. Thus, it becomes difficult for structured water molecules to pass into the macromolecular flake. This reduces the swelling of the flake and accordingly reduces the value of the characteristic viscosity. The second reason for the decrease in  $[\eta]$  may be an increase in the number of Na ions as a result of an increase in the degree of dissociation with an increase in temperature. An increase in the Huggins constant can also be considered as a logical consequence of the listed processes.

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<sup>1</sup> Ghebremedhin, M. Seiffert S., Thomas A.V. Physics of agarose fluid gels: reological properties and microstructure //Current Research in Food Science – 2021, v.4, – p.436–448.



a)



b)

Figure 1. Effect of sodium citric acid ( $C_6H_5O_7Na_3 \cdot 2H_2O$ ) at various concentrations (0.005 mol, 0.01 mol and 0.02 mol) on some studied parameters of the agarose-water system (a) intrinsic viscosity and b) Huggins constant.

Depending on the viscosity concentration, the critical viscosity concentration can be determined. For this, it is necessary to establish the concentration dependence of the characteristic viscosity in a wider concentration interval in a double logarithmic scale. Such a dependence for an aqueous solution of agarose at a temperature of 25 °C is presented in Figure 2. As you can see, the graph consists of two

straight lines with different slope coefficients. The concentration corresponding to the point of destruction gives the critical impurity concentration. As you can see, the critical concentration of agarose biopolymer for the formation of a gel in an aqueous medium at a temperature of 25 °C is  $C_{cr}=0.12\%$  by mass. We have to note that this value changes with the changing of temperature.

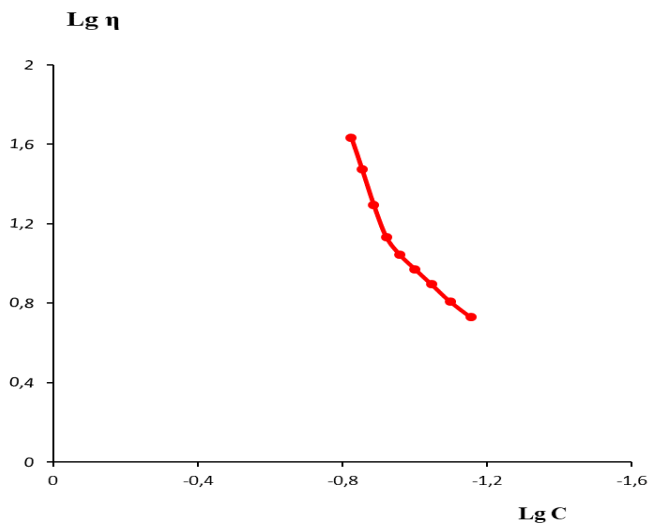


Figure 2. Determination of the critical concentration of agarose gelation at room temperature (at 25 °C)  $C_{critical}=0.12\%$  .

It is known that solutions of high molecular weight compounds, especially aqueous ones, are great importance from the application point of view. The application of solutions is closely related to their properties, and their properties, is related, to the structure which is formed as a result of the interaction of all components of the solution with each other. As a result of various external influences (temperature, pressure, additives, etc.), changes in the structure (at the same time properties) of the solution are manifested in the values of the physicochemical parameters that characterize it. Among the most important of these quantities are the activation parameters of viscous flow, which characterize the

rheological properties of the solution. The activation parameters of viscous flow are activation enthalpy, entropy and Gibbs free energy. It should be noted that the activation enthalpy characterizes the strength of the solution, determined by the interactions within it, and the activation entropy characterizes the regularity of the solution. It has been established that the activation enthalpy increases to a certain maximum at low temperatures and then decreases. This can be justified by the fact that water enter to the flake at low temperatures and can increase the strength of the solution due to the formation of certain bonds with segments of the macromolecule. However, as a result of the intensification of thermal movement with a subsequent increase in temperature, weak bonds are broken and the strength of the solution decreases, that is, the activation enthalpy decreases. But the activation entropy, on the contrary, decreases at low temperatures and increases at higher temperatures. At low temperatures, the regularity of the solution increases and the activation entropy decreases. As a result of the intensification of heat movement with a subsequent increase in temperature, the regularity of the solution decreases and the entropy of activation increases. The free activation Gibbs energy of a viscous flow depends linearly on temperature, so it increases with increasing temperature.

**Chapter IV** In this chapter, the microstructure of agarose gel and the changes caused by various additives in this microstructure are studied using dynamic light scattering and spectrophotometry methods.

Changes in agarose concentration and temperature affect the degree of association, which in turn affects the size of the particles which are consist of the gel structure. The size of these particles can change from a few nanometers to hundreds of nanometers. One method for accurately determining the particle size distribution in this range is the dynamic light scattering (DLS) method. The method is based on Brownian motion of small particles dispersed in a liquid. If all other parameters affecting the particle's motion are known, then the hydrodynamic radius can be determined by measuring the particle's speed.

Dynamic light scattering measurements were carried out on a Horiba Nano Partica SZ-100 on heating mode. The device gives a distribution of particle sizes that make up the gel structure.

First, it was studied how concentration affects the particle size distribution. Three concentrations of agarose forming a gel were considered: 0.2% (by weight) - weak gelation state; 0.5% (by weight) – medium gelation state; 1% (by weight) a strong gelation state. Measurements were carried out at a temperature of 25 °C after 1 hour of gel absorption. As a result of measurements, it was established that for a 0.2% agarose gel (weak gelation state), only large associates with sizes from 20 nm to 50 nm are present, and the distribution maximum corresponds to 33 nm, i.e. most particles in the gel structure are approximately this size. In addition to large associates, there are also small particles about 5-6 nm size at other concentrations (0.5% and 1%). With increasing concentration, the size of large particles increases (the most probable sizes are 33 nm, 75 nm and 210 nm, respectively), while the size of small particles does not change.

It has been established that the size of associates decrease with increasing temperature, that is, large associates, when heated, disintegrate into relatively smaller ones. It is observed small particles about 5 nm in addition with large particles starting from 60 °C. This means the formation of free bispirals or random flakes which are detached from associates.

Hydrophobic and hydrophilic additives can affect the number and size of particles which are consist of the gel, affecting the structure (the ratio of the number of free and bound water molecules) of the medium (water) in which the agarose gel is formed. Isoamyl alcohol and sodium salts of organic acids (mother acid and table salt) were chosen as hydrophobic and hydrophilic additives, respectively, and added to a 1% agarose gel in an amount of 0.5 mol; the resulting samples were studied by dynamic light scattering method.

Due to the obtained results, it can be noted that the hydrophilic additive sharply increases the size of associates, while the hydrophobic additive slightly reduces the size of associates. In

addition, hydrophilic additives eliminate free coils in the gel, which means that all coils participate in the association.

The investigation of agarose gel structure by spectrophotometric method confirms the previously obtained results. That is hydrophobic additives to structure the gel and shift the gelation and melting temperature upward. On the other hand hydrophilic additives, shift the gelation and melting temperature down.

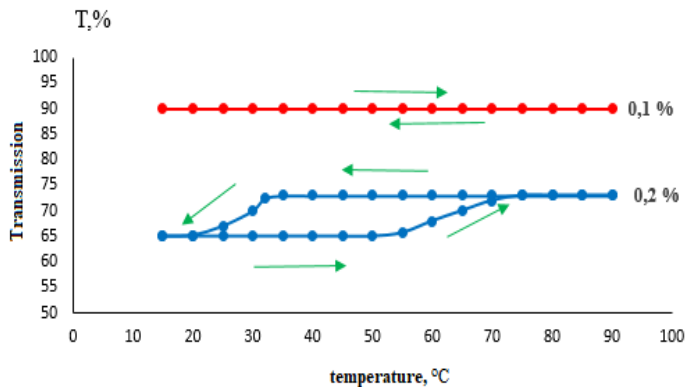
The concentration dependence of the transmission spectrum is considered. Measurements were carried out at several concentrations: a concentration that does not form a gel at room temperature (0.1%); weak gelation concentration (0.2%) and strong gelation concentration (1%). Transmission spectrum of the same concentration were obtained at different temperatures in both heating and cooling modes. As can be seen from the obtained results, with increasing temperature, the transmission of the gel increases to one or another degree, which is quite understandable. Based on general concepts, we can say that there happens crushing and dispersing of the particles which are considered scattering of light in gel with the increasing of temperature.

Note that a 0.1% agarose solution is a concentration that does not form a gel at room temperature. At this concentration, an absorption peak is observed at a wavelength  $\lambda_{\max} = 250$  nm. In our opinion, this peak is associated with sulfonamide groups of natural agar. Agarose is obtained from natural agar, and no matter how much it is purified, these groups remain in its composition in a certain amount. For the agarose used in our experiments, the critical gelation concentration is approximately 0.12%. Thus, in a 0.2% agarose concentration there is obtained a gel although it is weak. The scattering of light in gel space grid results with the reducing absorption peak as mentioned above. Where the concentration of agarose is high, for example 1% gel concentration this peak although is covered.

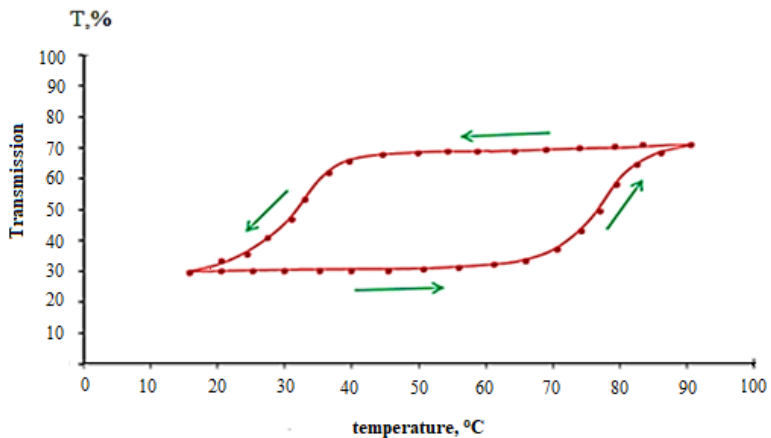
For to determine the gelation and the melting point, the temperature dependence of transmission for each concentration at a



certain wavelength ( $\lambda_{\max}=500$  nm) in two different mode- heated and cooled was constructed.



a)



b)

Figure 3. Temperature dependence of transmission on 500 nm for 0.1%, 0.2% (a), and 1% (b) concentrations of agarose gels in two different mode- heated and cooled.

As expected, thermal hysteresis appears at gelling concentrations, and the area of these hysteresis increase with the increasing of agarose concentration. Therefore, it is believed that the hysteresis area is a degree of thermal stability of the gel.

The hysteresis phenomenon which gelation ( $t_{\text{gel}}$ ) and melting ( $t_{\text{m}}$ ) temperatures sharply differs one of the characteristic properties of gel forming polymer solutions. The phenomenon of hysteresis is associated with the two-phase state of gels<sup>2</sup>. The phenomenon of hysteresis is associated with the completion of phase separation and has the nature of relaxation. During the gelation process, phase separation is completed, and at the same time the value of  $\Delta t = t_{\text{m}} - t_{\text{gel}}$  increases. However, at the gelation process  $t_{\text{m}}$  increases while the  $t_{\text{gel}}$  remains constant. During the gelation process, the increase in  $\Delta t$  is explained by the need for more intense heat motion for the formation of a perfect structure and the cooperative decomposition of this structure. The strong temperature hysteresis observed in the transmission spectrum of the agarose hydrogel suggests that, the formation and disintegration of the gel space grid occurs at different temperatures. Hysteresis is a logical consequence of the gelation and melting processes. While the formation of a gel involves the system going through a series of steps, its dissolution requires the simultaneous joint breaking of a number of bonds.

The hysteresis curves show that the association responsible for the formation of the space grid of the gel occurs at about 40 °C when the polymer solution is cooled. When the gel is heated, the dissolution of associates begins at 60-70 °C and covers a wide temperature range. As the concentration of agarose increases, the increase in the hysteresis area is mainly explained by the change in its height, i.e., the increase in the difference between transmission of the state sol and the gel. As the concentration increases, the transmission of the solution decreases, but the transmission of the gel decreases more than solution.

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<sup>2</sup> Ge, G. Wang Q., Zhang Y.Z. 3D Printing of Hydrogels for Stretchable Ionotronic Devices // *Adv. Funct. Mater.* – 2022, v.52, – p. 62 - 68.

The shape of the hysteresis shows that both the gelation temperature and the melting temperature of the gel increase with increasing concentration, but this increase is more for the melting temperature.

As the agarose concentration increases, the number of associated particles in the solution also increases. As a result of light scattering by associates, the transmission of the gel sharply decreases with increasing agarose concentration. An increase in temperature, as we said above, leads to varying degrees of fragmentation of associates in the gel (or solution). This leads to an increase in transmission of the gel (or solution) due to the weakening of light scattering.

The strong temperature hysteresis observed in the transmission of the agarose gel suggests that the formation and dissolution of the gel space grid occurs at different temperatures.

In many cases, the results of spectrophotometric measurements are given by optical density. Optical density is the absorption per unit length of the medium.

In Fig. Figure 4 shows the temperature dependence of the optical density of the agarose gel at various concentrations.

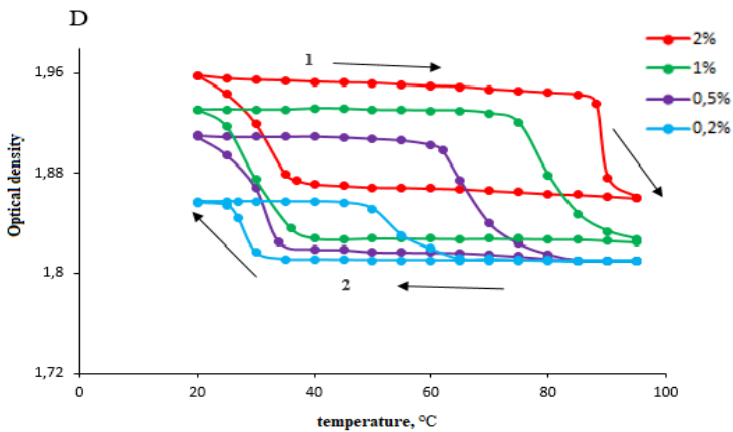


Figure 4. Temperature dependence of optical density of different concentrations of agarose gel.

The gelation ( $T_{gel}$ ) and melting ( $T_m$ ) temperatures are determined based on its hysteresis. Curve 1 on the graph represents the heating mode. Up to a certain temperature, the optical density does not change depending on the temperature, the dependence remains constant, after a certain temperature it begins to decrease. The point at which the optical density begins to decrease is the point at which the gel begins to melt ( $T_m$ ). The opposite of this process (curve 2) is the cooling mode. Here, as well as at a certain temperature, the optical density does not change depending on the temperature, but from a certain temperature it begins to increase. This temperature is considered the beginner of gelation temperature -  $T_{gel}$ . The area of hysteresis characterised the hardness of the gel. When the gel is heated, the dissolution of these associates occurs at a temperature of about  $60^{\circ}\text{C}$ , covering a wide temperature range. As the gel concentration increases due to an increase in the height difference of transmission, the hysteresis area also increases. Experimental results show that both the gelation state and the melting state temperatures of the gel increase with increasing gel concentration.

As the concentration of agarose increases, its strength rapidly increases too and characterized by an increase in the number of cross-links in the gel. As mentioned, the hysteresis area is a measure of thermal stability. When the concentration of agarose increases, the transmission decreases. This happens because small gel particles have combined to form larger particles - associates. These associations also combine to form a spatial network of the gel, and thus the light transmittance begins to decrease with increasing concentration.

Structural changes in polymer solutions are associated with changes in various types of interactions (hydrogen bonds, electrostatic, hydrophobic interactions, etc.) between the components of the system. This structure can be controlled by changing the shares given by the components of the solution to structural changes, in other words, existing interactions, and in a particular case, to obtain gels whose properties are already known. One of the ways to change the structure and properties of a solution is to add low-

molecular compounds (salts, acids, sugars, alcohols, etc.), which have a screening effect on various interactions in the system. For this purpose, by adding a number of low-molecular hydrophilic compounds, citric, succinic and tartaric acids (0.5 mol) to an agarose-aqueous solution of sodium salts (0.5 mol), their effect on the gelling and melting points was studied.

The influence of sodium salts of citric, tartaric and succinic acids on the gelation ( $t_{gel}$ ) and melting ( $t_m$ ) temperatures in different concentrations of agarose gel was studied. As a result of the investigations, it was found that compounds containing both hydrophilic and hydrophobic functional groups have a weak effect on the  $t_{gel}$  and  $t_m$  values. It can be considered that this effect is associated with the effect of dissociation of hydrogen bonds of ions formed as a result of the dissociation of the listed compounds and the structuring effect of their hydrophobic groups on water.

The effect of a number of inorganic salts (NaCl, KCl, KBr, CaCl<sub>2</sub>) and isoamyl alcohol on the (1%) concentration of agarose was also studied. The NaCl, KCl and CaCl<sub>2</sub> salts of these additives are hydrophilic, while the KBr salt and isoamyl alcohol are hydrophobic.

It was found that the gelation ( $T_{gel}$ ) and melting ( $T_m$ ) temperatures were significantly increased by influence of salts. The destructive or structuring effect on the structure of water as a result of the hydration of ions which are considered salts included in the agarose-water system is also manifested in the transmission spectrum.

As it is known, the influence of inorganic salts on the structure of water depends on the ability of the ion to polarize water, which, in turn, depends on the size and charge of the ion, more precisely, the surface charge density of the ion. Ions with a high surface charge density have a structuring effect on the surrounding water, and ions with a low surface charge have a destructive effect. A change in the structure of water determines whether various types of bonds (dipole-dipole interaction, hydrogen bonds, etc.) necessary for the formation of a gel can be formed in a solution of a polymer in water. The effect of organic salts on the gelation process in the agarose-water system is

associated with which of the hydrophobic and hydrophilic functional groups of these salts is more influence to water structure.

**Chapter V**, the electrical and dielectric properties of the gel are described using coul-coul diagrams which is obtained from the temperature dependence of conductivity and the dependence of the real and imaginary parts of the dielectric constant on each other.

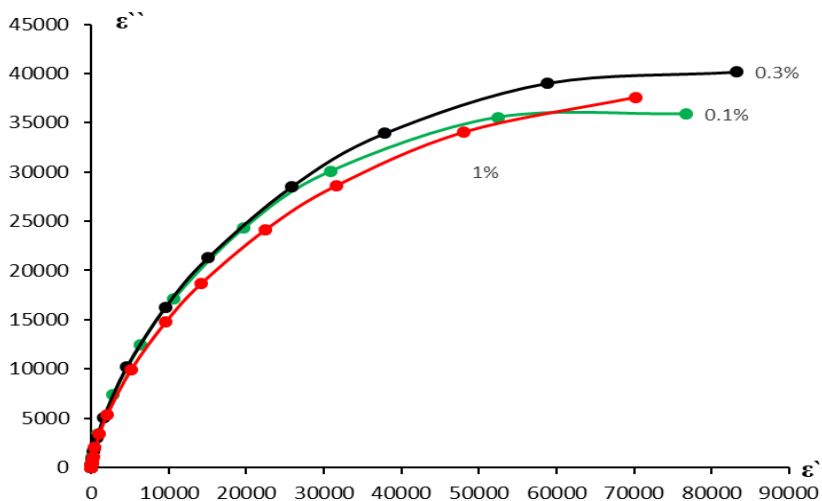


Figure 5. Debye diagrams of agarose-water system at different concentrations at 25 °C.

From the analysis of the graphs it is clear that dielectric dispersion for a 0.1% solution occurs at a frequency of about 20 Hz. For 0.3% - 1% solutions, we can only say that the relaxation of the dielectric constant occurs at lower frequencies, and its value cannot be accurately determined, since it goes beyond the frequency range of the device (20 Gs - 1 MGs).

The observed relaxations, in our opinion, are associated with the movement of charged associates (large-sized ions) in the double layer formed near the electrodes. Since 0.3% and 1% solutions are in the form of a gel, vibrations of charged associates in an alternating

electric field “freeze” at lower frequencies, since the viscosity of the gel is very high due to the existence of a space grid.

In the case of a 0.1% solution (sol) in a spherical approximation, the size of these associations can be estimated using formula (1):

$$\tau = \frac{4\pi\eta R^3}{kT} \quad (1)$$

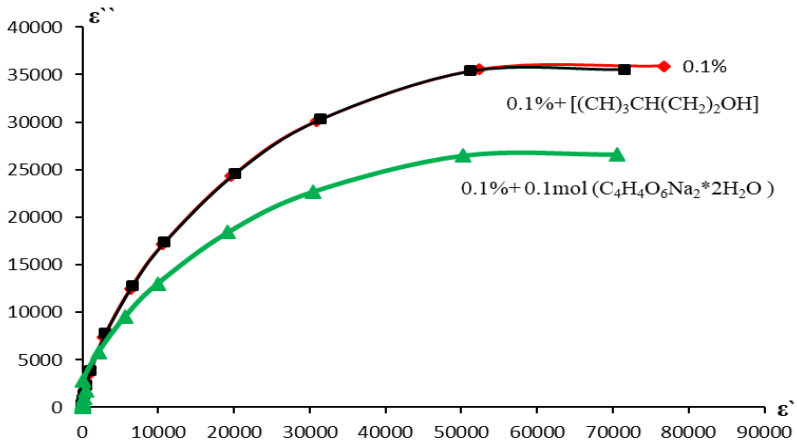


Figure 6. Debye diagram for 0.1% aqueous solution of agarose in pure form and with hydrophobic (isoamyl alcohol) and hydrophilic additives Na salt of tartaric acid ( $C_4H_4O_6Na_2 \cdot 2H_2O$ ).

As can be seen from Figure 5, in a 0.1% solution, where a gel cannot form, hydrophobic additives practically do not change the  $\epsilon'(\epsilon'')$  dependence. It means that a hydrophobic additive does not significantly change the association in the sol state of solution. A hydrophilic additive slightly reduces the time dispersion, while the concentration of agarose in water differs slightly (0.3% and 1%). It is clear seen from the figure 7 and 8 that, , the hydrophobic additive does not have or has a weak effect on the dielectric dispersion of the gel and the size of the charged associates at two concentrations. Also it is seen from the graph that the hydrophilic additive shifts the dielectric dispersion towards lower frequencies.

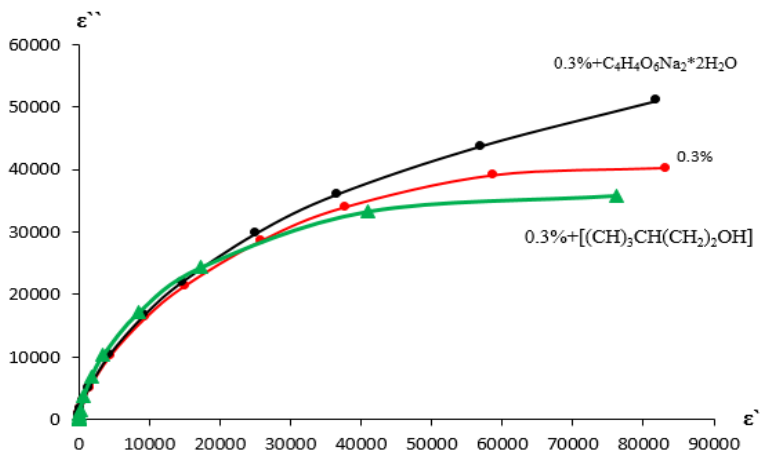


Figure 7. Debye diagram for 0.3% concentration of agarose in pure form, with hydrophobic (isoamyl alcohol) and hydrophilic Na salt of tartaric acid ( $C_4H_4O_6Na_2 \cdot 2H_2O$ ) additives.

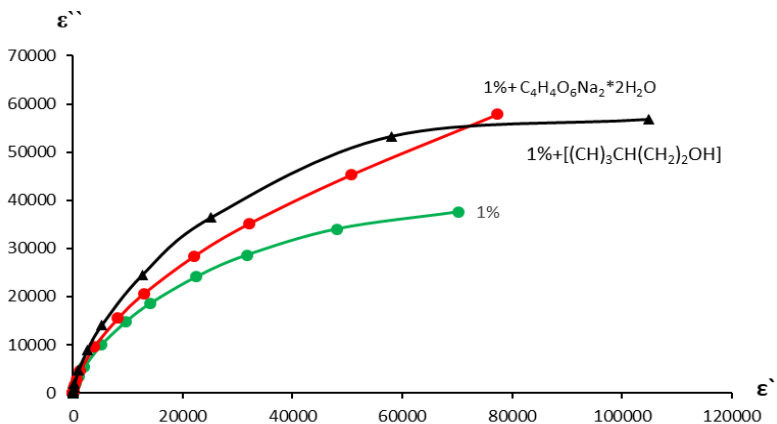


Figure 8. Debye diagram for 1% concentration of agarose in pure form, with hydrophobic (isoamyl) and hydrophilic Na-salt of tartaric acid ( $C_4H_4O_6Na_2 \cdot 2H_2O$ ) additives.



Studying the electrical conductivity of polymer gels provides certain information about their structure. In addition, since the electrical conductivity in the region of phase transitions undergoes serious changes, measuring the electrical conductivity makes it possible to determine the points of phase transitions with a certain accuracy.

The dependence of agarose gel conductivity on agarose concentration, temperature, also the influence of hydrophilic and hydrophobic additives on these dependencies was studied. Isoamyl alcohol ( $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{OH}$ ) in an amount of 1% by weight was used as a hydrophobic additive, and sodium salt of tartaric acid ( $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 \cdot 2\text{H}_2\text{O}$ ) was used as a hydrophilic additive.

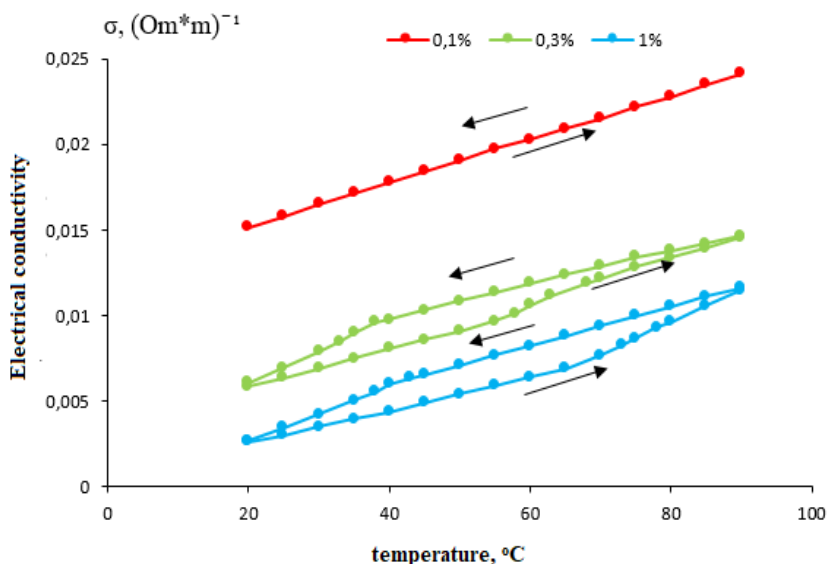


Figure 9. Temperature dependence of electrical conductivity of agarose gel at different concentrations.

In Fig. Figure 9 shows the temperature dependences of the electrical conductivity of the agarose gel at various concentrations in both heating and cooling modes. The 0.1% agarose solution did not form a gel, that is why the dependence had no hysteresis.

Although agarose hydrogel is a thermally reversible gel, there is strong thermal hysteresis in its physical properties. That is, during heating and cooling, the values of the physical quantities characterizing the gel (emissivity, flow voltage, electrical conductivity, etc.) do not coincide at the same temperature. This can be described in 0.3% and 1% solutions (curves 2 and 3 in Fig. 8).

These curves can be characterized as follows. When the gel is heated, starting from room temperature, its electrical conductivity increases (Fig. 9). At a certain temperature (60-75 °C) this increase occurs with a slight jump. Obviously, this is due to the disintegration of the space grid of the gel. This temperature is called melting temperature of the gel or the gel-sol phase transition temperature ( $T_m$ ). When the obtained solution (sol) is cooled from 90 to 95 °C, the conductivity decreases, but the curve passes through the top, since the space grid is not restored at the temperature at which it dissolves. The restoration of the space grid occurs at very low temperatures (at 30-40 °C), which is again accompanied by a weak jump in the decrease in conductivity. This jump is associated with the sol-gel phase transition and the corresponding temperature is called the transition temperature ( $T_g$ ).

Thus, according to curves 2 and 3, the gelation temperature is  $T_g = 35^\circ\text{C}$  for 0.3% weak agarose gel and  $T_g = 40^\circ\text{C}$  for 1% strong gel. The melting point of 0.3% gel is  $T=65^\circ\text{C}$ , and 1% gel  $T=75^\circ\text{C}$ .

Figure 10 shows the dependence of the electrical conductivity of an agarose solution on the concentration of agarose at a temperature of 25 °C.

As expected, conductivity decreases with increasing concentration. The main reason of this is that when polymer concentration increases the mobility of ions will be decrease in a result of the increase in solution viscosity. Another reason is a decrease in the mobility of ions as a result of compression of the

cores of the space grid with increasing concentration, when the solution is in the form of a gel.

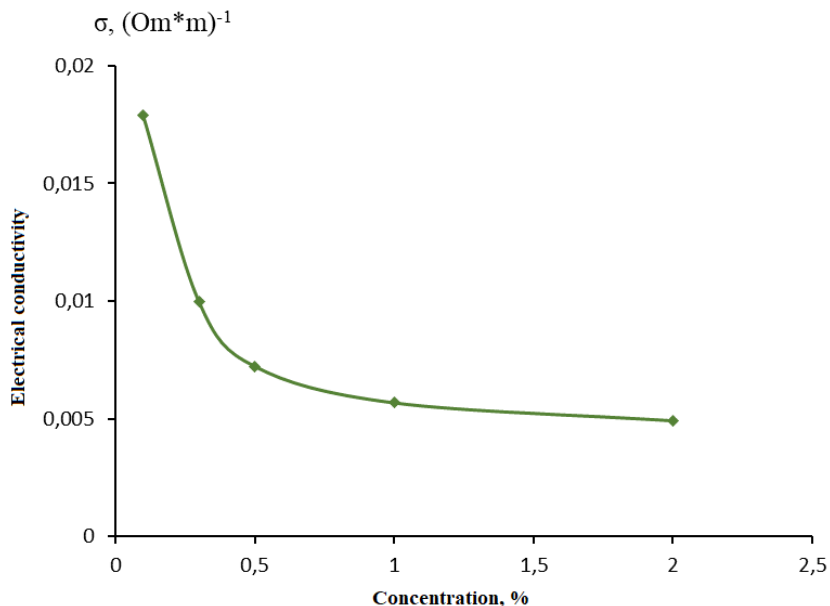


Figure 10. Dependence of electrical conductivity of agarose gel on agarose concentration.

It is known from the temperature dependences of the electrical conductivity of 1% agarose gel and 1% gel with hydrophobic and hydrophilic additives, that the conductivity of the gel increases in both cases (fig.11). A hydrophobic additive increases conductivity by 2–3 times, and a hydrophilic additive increases conductivity by at least an order of magnitude. In addition, hydrophobic and hydrophilic additives shift the melting and gelation temperatures of the gel in opposite directions. For example, adding 1% isoamylic acid (hydrophobic) to a 1% agarose gel reduces the gelation temperature from 40 °C to 36 °C, and the melting temperature of the gel from 75 °C to 73 °C, that is, the hydrophobic additive weakens the gel. Adding 1% Na salt of tartaric acid to 1% agarose gel increases the gelation temperature from 40 °C to 45 °C, and the

melting temperature of the gel from 75 °C to 82 °C, that is, the hydrophilic additive strengthens the gel.

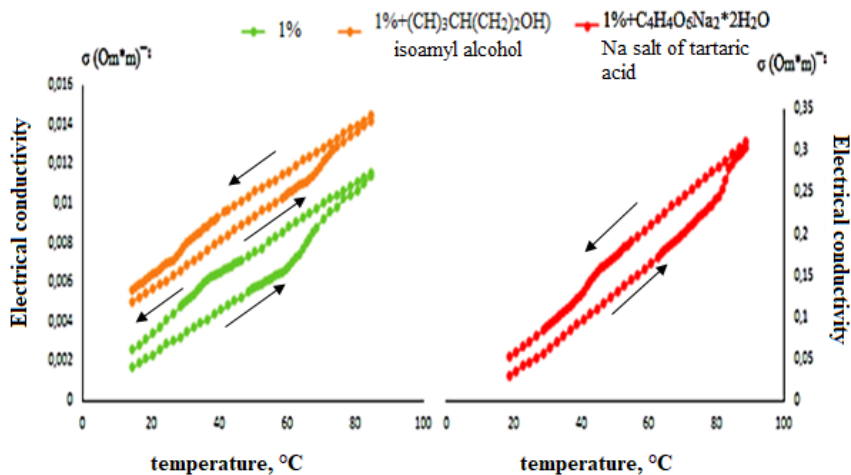


Figure 11. Effect of hydrophobic and hydrophilic additives of agarose gel on electrical conductivity.

### MAIN RESULT PRESENTED FOR DEFENCE

1. Based on viscometric measurements, it was established that the extrema observed due to the influence of various additives on the temperature dependence of the intrinsic viscosity ( $[\eta]$ ) and Huggins constant ( $k'$ ) of aqueous solutions of agarose correspond to different temperature values. These maximum (or minimum) temperatures are considered to be the transition temperatures from the static flake conformation state to the rigid stick conformation state.
2. Rheological methods have shown that increasing the concentration of agarose in the gel leads to an increase in the yield stress and the lowest Newtonian viscosity. The yield stress value was significantly increased by the KCl salt, and the viscosity by the CaCl<sub>2</sub> salt.
3. Thermal hysteresis properties studied from the transmission spectra of agarose gels suggest that the degree of hysteresis, that

is, the difference between the melting and gelation temperatures of the gel, increases with increasing agarose concentration. It is shown that hydrophobic salts shift the boiling and melting points upward, while hydrophilic salts, on the contrary, shift the boiling and melting points down.

4. Using low-frequency dielectric spectroscopy, it was established that hydrophobic additives weakly change the dielectric relaxation of an agarose gel, while hydrophilic additives shift it to the low frequency region. This is due to a change in the viscosity of the solution.
5. The investigations by dynamic light scattering method show that the size of associates increases with increasing agarose concentration, and the size of pores in the space grid of the gel decreases. For this reason, it becomes difficult for small particles to penetrate from one pore to another, and the diffusion coefficient decreases. Additives of a hydrophilic nature sharply increase the size of associates, and additives of a hydrophobic nature, on the contrary, slightly reduce the size of associates. In addition, additives of a hydrophilic nature destroy free coils in the gel
6. Conductometric measurements show that the conductivity in the agarose-water system is caused by ions  $H^+$  and  $OH^-$ , formed as a result of water dissociation, and some charged radicals associated with incomplete purification of agarose biopolymer. Additives of a hydrophobic nature increase the conductivity by 2-3 times, and additives of a hydrophilic nature increase the conductivity by at least an order of magnitude. The observed thermal hysteresis of the temperature dependence of the conductivity also shows that hydrophobic and hydrophilic additives shift the melting and gelation temperatures of the gel in opposite directions.

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The defense of the dissertation will be held on September 27, 2024 at 15<sup>00</sup> at the meeting of the ED 2.19 Dissertation Council operating under Baku State University.

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Avtoreferat Abstract was sent to the required addresses on 28 iyun  
2024

Signed for print:24.06.2024

Paper format: A5

Volume: 37160

Number of hard copies:20