STUDY OF SOL-GEL PHASE TRANSITION IN THE AGAROSE-WATER SYSTEM BY ELECTRICAL CONDUCTIVITY

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In the present work the electrical conductivity method was used to study the sol-gel phase transition in the agarose-water system. The 0.1% agarose-water system is used for this purpose; The temperature dependence of the conductivity of 0,1%, 0.3% and 1% solutions and as well as the influence of hydrophobic (isoamyl alcohol) and hydrophilic (Na salt of tartaric acid) additives on this dependence were studied.It was shown that the hydrophilic additive makes the gel more stronger and shifts the gelation (Tg) and melting (Te) temperatures up. The hydrophobic additive (hydrophobic isoamyl alcohol) on the contrary weakens the gel and shifts the gelation (Tg) and melting (Te) temperatures downward.

Keywords: polymeric hydrogels, agarose, electrical conductivity, hydrophobic additive, hydrophilic additive.
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INTRODUCTION

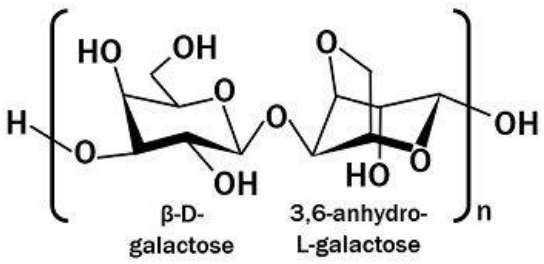
Polymers (and their alloys) can be divided into two types according to their electrical conductivity: neutral and charged polymers [1,2]. Examples of neutral polymers among the natural polymers are gelatin and agarose. Gellan, carrageenan, etc. biopolymers related to the charged biopolymers [3]. The solution of these biopolymers in water becomes a gel above a certain concentration (xg) and below a certain temperature (Tg), that is, it retains its shape (loses fluidity) under small mechanical influences. This feature of the gel is associated with the presence of a three-dimensional spatial network, in the core of which water is immobilized, and opens the way to numerous applications [4].

The study of electrical conductivity in polymer gels carries some information about their structure [5]. In addition, since electrical conductivity around phase transitions undergoes a significant change, the measurement of electrical conductivity makes it possible to determine the points of phase transitions with some accuracy. Conductivity studies in such systems play an important role when choosing a model to study electrical properties of the brain or the effect of electric fields on the central nervous system [6].

It was mentioned above that agarose, a typical representative of natural polysaccharides, is an uncharged (neutral) polymer and possesses many useful properties: bioabrasiveness, biocompatibility, strong thermally reversible gel-forming ability, etc. Due to these properties, agarose is now successfully used for drug delivery to the target organ [7,8] and in tissue engineering [9]. When applied, it is necessary to adapt the physical (mechanical, thermal, electrical, etc.) of the agarose gel to the required values, which is achieved by changing the agarose concentration and adding additives of different nature to the gel. In fact, this is done by modifying the gel structure. It was mentioned above that the study of electrical conductivity plays a role in the study of gel structure. The present work studied the dependence of agarose gel conductivity on agarose concentration, temperature, and the influence of hydrophilic and hydrophobic additives on these dependencies.

EXPERIMENT

Agarose is the main component of red algae agar, and its monomer (agarobiose) has the following chemical structure [9]:



The agarose gel was prepared as follows [10]. Agarose powder was weighed on ADAM PW 124 (USA) (accuracy 0.1 mg) and added to bidistilled water. After 1 day of storage (swelling process), the mixture is heated to 95°C. The samples are poured into a glass bath containing platinum electrodes in the form of a solution (sol) and cooled to room temperature. The area of the platinum electrodes is 1 cm2 and the distance between them is 0.2 cm. Isoamyl alcohol ($(CH_3)_2CH(CH_2)_2OH$) was used as a hydrophobic additive in an amount of 1% by weight, and Na-salt of tartaric acid ($C_4H_4O_6Na_2{*}2H_2O$) was used as a

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hydrophilic additive. The electrical properties of the agarose gel were measured on an IET 1920 LCR meter (USA) at a frequency of 2 kHz. The measuring voltage (test signal) applied to the sample was 0.5 V. In an AC circuit, when the liquid dielectric is poured into a bath with platinum electrodes, it can be considered as a capacitor of capacity C and a resistor of resistance R connected in parallel. In this case the electrical conductivity is calculated by the following formula:

$$\sigma = \frac{d}{RS}$$

Here S is the area of the electrodes, and d is the distance between the electrodes.

Temperature was measured using a chromel-alumel thermocouple. The temperature generated at the thermocouple outlet was measured with an EHQ B7-21 microvoltmeter (Russia). When the solution is in gel form, measurements are taken after holding for at least one hour at each temperature because agarose gel takes a long time to reach thermodynamic equilibrium. Therefore, a GL-100 thermostat (China) was used to ensure temperature stability during measurements.

RESULTS AND THEIR EXPLANATION

The results of measurements are presented in graphs 1-4. Figure 1 shows the temperature dependences of the electrical conductivity of the agarose gel at different concentrations in both the heating and cooling modes. Since the 0.1% agarose solution did not form a gel, the dependence showed no hysteresis. The critical concentration of agarose for gel formation is about 0.15% [11]. Although the agarose hydrogel is a thermally reversible gel, there is a strong thermal hysteresis in its physical properties. That is, when heated and cooled, the values of the physical quantities characterizing the gel (radiation coefficient, flux voltage, electric voltage, etc.) do not overlap at the same temperature. Confirmation of this can be seen in 0.3% and 1% solutions (curves 2 and 3 in Fig. 1). These curves can be characterized as follows. When the gel is heated from room temperature, its electrical conductivity increases. At a certain temperature (60-80°C) this increase occurs with a small jump. Obviously, this is due to the disintegration of the spatial mesh of the gel. This temperature is called the gel melting temperature or the temperature of the gel-sol phase transition (T_m). When the resulting solution (sol) cools from 90 to 95 ˚C, the conductivity decreases, but the curve goes over the top because the bulk network is not restored. Recovery of the spatial network occurs at very low temperatures (30-40 ˚C), which again is accompanied by a weak jump in the decrease of conductivity. This jump is associated with the sol-gel phase transition, and the corresponding temperature is called the transition temperature (Tg). Thus, according to curves 2 and 3, the gel formation temperature is T_g = 35°C for a 0.3% weak agarose gel and T_g = 40°C for a 1% strong gel. The melting temperature of the 0.3% gel T=65°C and the 1% gel T=75°C.

Figure 2 shows the dependence of the conductivity of agarose solution on the concentration of agarose at 25 ˚C. As can be seen, the conductivity decreases with increasing concentration. The main reason for this is that the mobility of ions decreases with increasing polymer concentration as a result of increasing solution viscosity. Another reason is the decrease in ion mobility as a result of the compression of the spatial network nuclei as the concentration increases, when the solution is in the form of a gel.

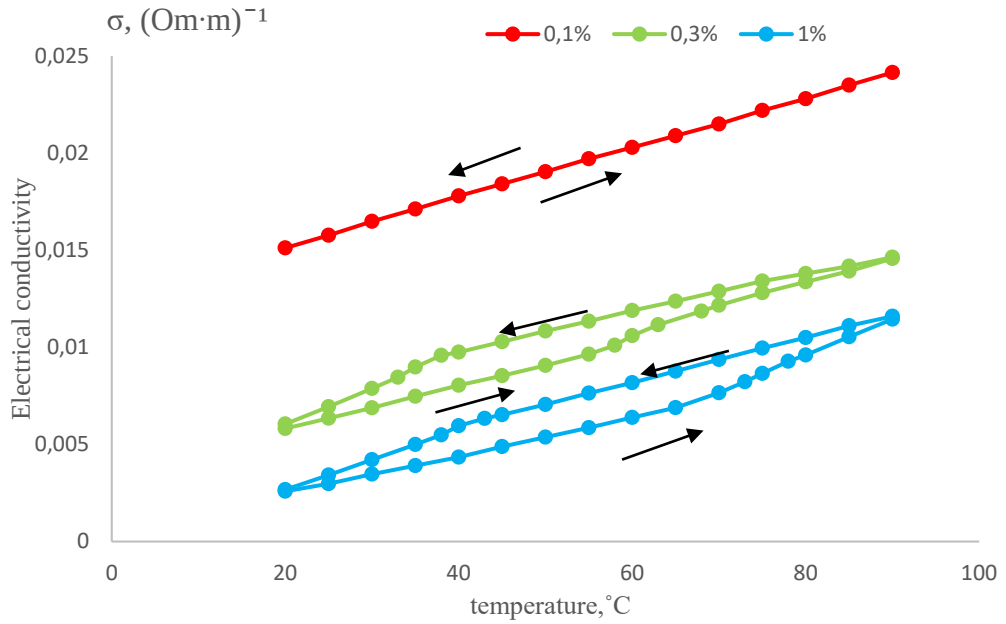

Fig.1. The dependence of electrical conductivity on temperature for different concentrations of agarose-water systems.

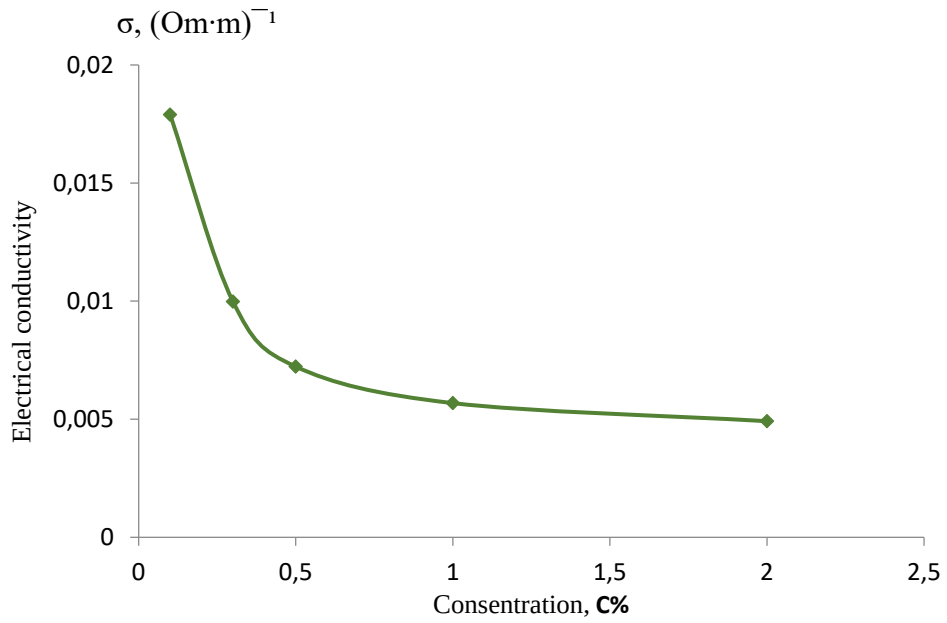

Fig.2. The dependence of agarose gel conductivity on the consentration of agarose-water systems.

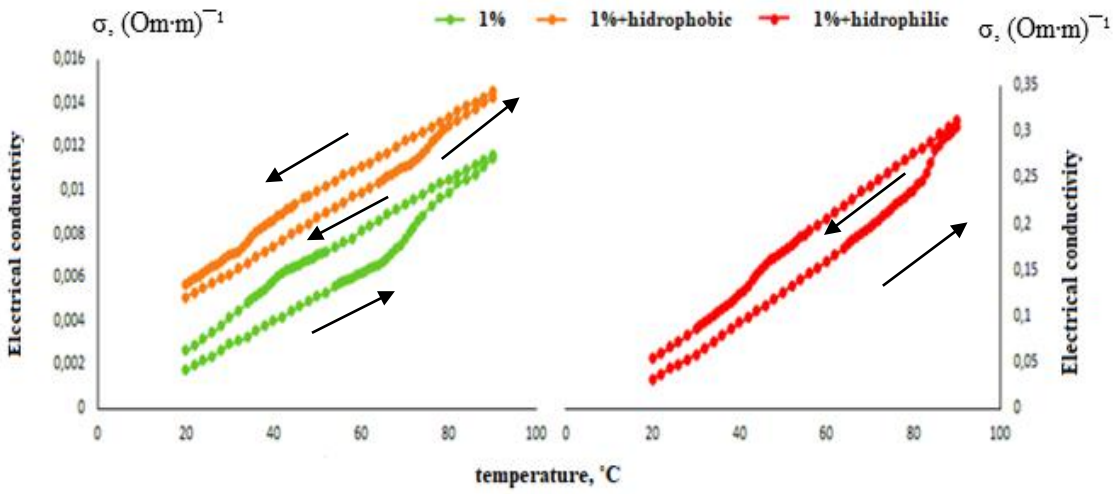

Fig. 3. The effect of hydrophobic (isoamyl alcohol) and hydrophilic (Na salt oftartaric acid) additives on the agarose gel on electrical conductivity.

Fig. 3 shows temperature dependences of electrical conductivity of 1% agarose gel and 1% gel with hydrophobic and hydrophilic additives. In both cases the gel conductivity increases. Hydrophobic additive increases the conductivity by 2-3 times, and hydrophilic additive increases the conductivity by at least one compilation.

In addition, hydrophobic and hydrophilic additives shift the gel melting and gelation temperatures in opposite directions. For example, when 1% isoamyl alcohol (hydrophobic) is added to 1% agarose gel, the gelation temperature decreases from 40 ˚C to 36 ˚C and melting temperature decreases from 75 ˚C to 73 ˚C, so the hydrophobic additive weakens the gel. Adding 1% sodium salt of tartaric acid to 1% agarose gel, the gelation temperature increases from 40 ˚C to 45 ˚C, and the melting temperature of the gel from 75 ˚C to 82 ˚C, so the hydrophilic additive makes the gel more stronger.

The results for all graphs-the temperature dependence of agarose concentration and the temperature dependence curve of electrical conductivity at each concentration when the hydrophobic and hydrophilic additives are added-are summarized in Table 1. It should be noted that T_g and T_m determined by the coductometric method and this results differ by 1-2 ˚C with the results of the optical method.

Table 1.

C %	Agarose gel, t_g (˚C)	Agarose gel, t_m (˚C)	Agarose gel + hydrophilic additive t_g (˚C)	Agarose gel + hydrophilic additive t_m (˚C)	Agarose gel + hydrophobic additive t_g (˚C)	Agarose gel + hydrophobic additive t_m (˚C)
0.1	–	–	30	45	-	-
0.3	35	58	40	70	31	61
0,5	36	60	39	66	33	58
1	40	75	45	82	36	73
2	41	88	46	90	38	86

Electrical conductivity in the agarose-water system occurred due to the dissociated H^+ and OH^- ions of water and some ionic additives (charged radicals) due to incomplete purification of agarose biopolymer. It should be noted that the amount of these ions is very less, that is why the given porsion of water to the conductivity is more greater.

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