

THE INVESTIGATION OF GELATINCREATION PROCESSES IN THE SYSTEM OF AGAROSA-WATER-CARBAMIDE

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In the given paper the influence of carbamide on the gelatincreation process on the structuring in the water agarosa solutions with the use of the dispersion method of the optical density, has been studied. The temperature dependences of the optical density at the cooling of the solutions and heating of gelatins are obtained. The temperatures of gelatincreation and melting, sizes and number concentration (particle number in the volume unit) of the submolecular particles, are obtained. It is established, that carbamide dumps the gelatincreation process, shifting the temperatures of the melting and the beginning of the gelatincreation to the region of more low temperatures. Carbamide, destroying the intermolecular and helium communications, the water structure, weakens the gelatin strength.

Key words: agarosa, carbamide, water solutions, gelatincreation, structuring, gelatincreation temperature, melting temperature, gelatin strength, hysteresis.

The solutions of some polymers at the definite concentration and conditions have the possibility of the gelatincreation. This takes place after the achieving of such state, at which the energy of the polymer interaction with the solvent becomes less, than the energy of macromolecul interaction [1]. In the result between macromolecules, and between their associates and agregates also are the local communications, leading to the grid creation. At the detail considering of the gelatin structure it is need to take into consideration, that the submolecular structures of the fluctuation character with the different continuous of "life" appear besides of the stable compounds in the polymer systems. Gelatins, formed by polymer solutions at the change of the temperature and composition are heterogeneous and that's why they have the such high light scattering, as the colloid systems. In the dependence on the gelatincreation conditions, the number and size of dispersion phase particles change and the light scattering intensity changes correspondingly. The gelatin of the solutions of many polymers can be achieved by the addition of the precipitant to them, and at the change of the chemical composition of the solved polymer, also. In all these cases the gelatin takes place in the result of the system transition in the state of the limited compatibility of the polymer with the solvent.

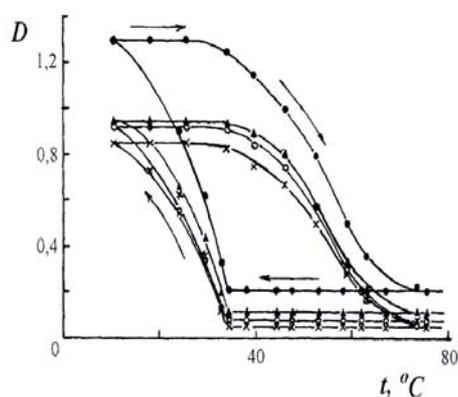


Fig.1. The temperature dependences of optical for 1% agarosa solution at the different wave length: ● - 400, ▲ - 490, ○ - 540, x - 670.

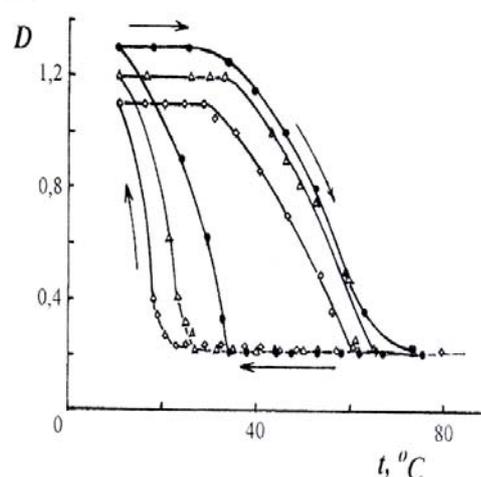


Fig.2. The temperature dependences of optical density of 1%water agarosa solutions without (●) and at the carbamide addition: 1M(Δ) and 3M(◇) $\lambda=400\text{nm}$.

In the given paper the gelatin of the water solutions of the one from the gelatincreating polymers is considered, especially agarosa at the change of the temperature and solvent composition. Using the concentration photoelectric calorimeter (KFK-2), the temperature dependences of the optical density of the (D) solutions, given on the fig.1 with the dependence $D=f(t^\circ)$ for 1% agarosa solution at the different wave lengths, were fixed. (Such dependencies had been obtained for the rest solutions).The agarosa concentration was kept constant -1%, but carbamide concentration, used as the addition, was 1,5 and 3 moles. The dependencies $D=f(t^\circ)$ for the all investigated solutions at $\lambda=400\text{nm}$ were given on the fig.2. The technique of investigation is described in [2]. The temperature dependences of the optical density were obtained as at the cooling from $\approx 80^\circ\text{C}$ till the room temperature, so at the heating from the room temperature till the gelatin melting temperature (t_{mi}). These temperature dependences don't combine, but they create the hysteresis loops, because of the discombination of the gelatin and melting temperature. It is well known [3] that in always gelatincreating system the melting temperature is higher, than gelatin temperature (t_{gel}). The hysteresis reason of the melting and gelatin is in the clear difference of the mechanisms of the creation and melting of the gelatins. The gelatin creation takes place

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through the consequence of many steps, demanding the definite cooling and time, but melting of the gelatin has all signs of the cooperate transitions. The system turbidity increases at the agregiroation and creation of the grid points. In the overwhelming majority of the gelatins the grid points are created by submolecular elements or so-called by the submolecular particles (SMP), the sizes of which change with the temperature and solvent nature. For the defining of the R sizes and number concentration of N particles (number of particles in the volume unit), the method, worked by Clenin with collaborations [4] on the base of Mi theory and being in the optical density measurement at the different wave lengths of the fallen light, is used.

Taking into consideration the experimental data, we can say the following. According to the generally accepted Ris model for the polysaccharides [5], one of which agarosa is, macromolecules in the solution at the high temperatures are rolled in balls. They unroll at the temperature decreases and create the spirals, later bispirals. These bispirals join in the aggregates (SMP). As at the high temperatures the optical density doesn't change, so it is clear, that sizes of these particles are small yet. The SMP increase at the temperature decrease, and when their size becomes enough, the turbidity takes place, at which is equal to the strong increase of the optical density (fig.1 and 2). In this time the first local communication between SMP appear, i.e. the rudiments of the space gelatin grid also appear. This is equal to the bendings on the cooling curves $D=f(t^\circ)$. Temperature, considering to such is the temperature, beginning with which the creation of gelatin (t_{gel}) is possible. At the later temperature decrease the number of communications increases, leading finally to the creation of the gelatin grid. For the clarity t_{gel} was fixed also by kinetic dependencies of the optical density $D=f(t^\circ)$, where t is time. Moreover, the D values in the bending region were taken through 1°C or 0,5°C. For example, in the paper the such dependencies

$D=f(t^\circ)$ for 1% solution of agarosa (fig. 3) are given. As it is seen from the fig.3, the optical density at the temperatures, which are higher, than t_{gel} , is kept constant. But at the first signs of gelatin creation, i.e. at $t \leq t_{gel}$, the temperature becomes change with time. After the full forming of the gelatin, the optical density again stays constant with the time change.

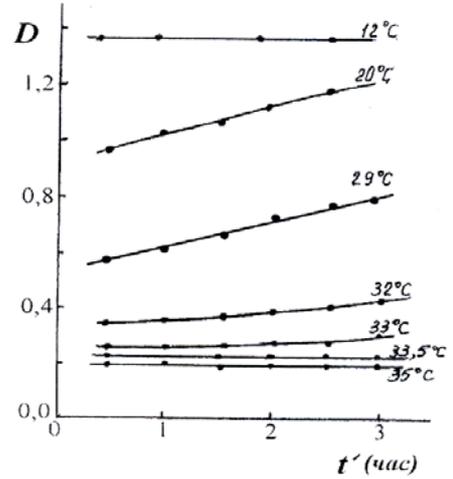


Fig.3. The kinetic dependencies for 1% water agarosa solution at $\lambda=400\text{nm}$

If we consider the heating curves, that it is seen on them, that with the temperature increase the optical density firstly doesn't change till the definite temperature, considering to the be beginning of the gelatin destruction, but later it decrease till the temperature of full gelatin melting (t_{mel}), at which the optical density becomes equal to D at high temperatures, from which the measurements of cooling curves had begin. The defined by such way, t_{gel} and t_{mel} are given in the table 1.

Table1
System:1% agarosa+water+carbamide

Concentration of carbamide, mole	Squares of hysteresis, S_h				t_{gel} , °C	t_{mel} , °C
	$\lambda=400$	$\lambda=490$	$\lambda=540$	$\lambda=670$		
-	31.9	27.65	24.1	23.6	33.0	73.5
1.5	30.3	26.73	22.9	22.48	26.5	66.0
3.0	29.3	24.55	21.1	21.78	21.0	60.0

On the base of the experimental data and according to the ref [4], the sizes of SMP and their number concentration in the dependence on the temperature for all investigated solutions, taking into consideration the optical density values, obtained at the cooling of the solutions, had been calculated. The temperature dependences of values R and N are given on the figures 4-6. From the figures it is seen, that dependencies $R=f(t^\circ)$ are analogical to the dependencies $D=f(t^\circ)$. In the high temperature region the particle sizes stay constant, but beginning from the some temperature $t \leq t_{gel}$, the growth of these particles, which continues till the room temperature, when solution transfer to gelatin, takes place. For the SMP number the inverse dependence is observed, i.e. if there are polymer chains join, so there are many R , and there are less N .

Let's consider the influence of the carbamide on the gelatincreation process in the water solutions of agarosa. It is known, that carbamide destroys the water structure, increasing the part of water in the monomolecular state, and by this increases the growth of its activity as solvent [6.7]. The creation of stable helium communications of water molecules with carbamide molecule, leads to the such orientation of water molecules, which difficulties the creation of the helium communications in the solvent and this is caused the water structure destruction. In the ref [8] for the water solutions of carbamide the structure temperatures (T_{str}), characterising the degree of the solution structuring in respect to the pure water, are defined. The structure temperatures, given in the ref [8] for the carbamide water solutions in the wide interval of its concentrations, decrease from T_{str} for pure water ($\approx 147^\circ\text{K}$) till 0°K at carbamide

concentration, which is equal to 10 moles, that proves about decrease of water structuring with the increase of carbamide concentration till full destroying at 10 moles of carbamide. The investigation of 0,1% solution of agarosa, not creating the gelatin [8], shows, that with the addition of carbamide (from 1 till 8 moles), the structure temperature of solutions decreases and although T_{str} of agarosa solutions is higher than T_{str} for pure water at carbamide concentrations 1,5 and 3

moles, it becomes lower, than T_{str} for the agarosa water solution without carbamide (table2). This says about that although carbamide destructures the water and increases of its solving capability, that leads to the T_{str} of agarosa water solutions with carbamide, but agarosa itself keeps some structuring capability to the water, and weakens the carbamide action on the water.

Table 2
System: Agarosa (0,1%)+carbamide+water(data of ref [8])

Carbamide concentration, mole	Structural temperature of carbamide water solutions T_{str}, K	Structural temperature of agarosa water solutions with carbamide T_{str}, K
-	147	253
1	135	193
1.5	126	180
3	110	154
5	88	138
7	65	130
8	55	114

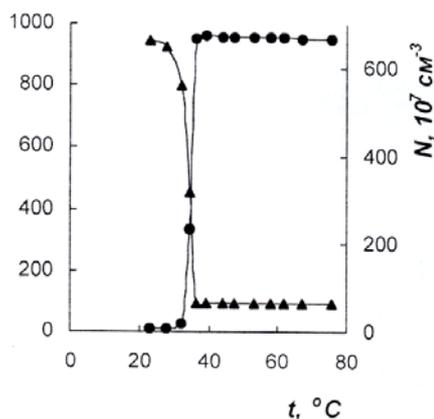


Fig.4. The temperature dependencies of R and N for 1% water agarosa solution.

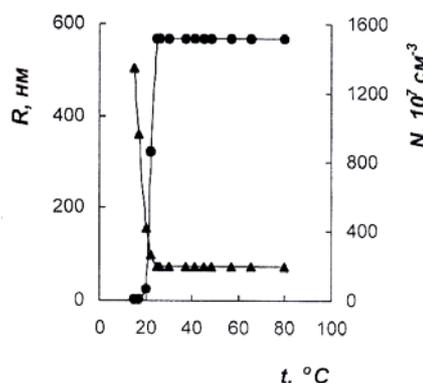


Fig.6. The temperature dependencies of R and N for 1% water agarosa solution at the presence of M carbamide.

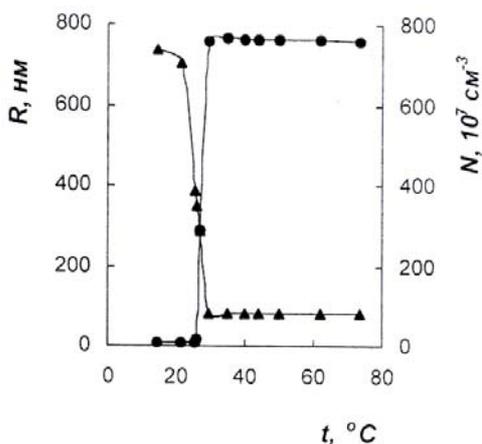


Fig.5. The temperature dependencies of R and N for 1% water agarosa solution at the presence of 1,5M carbamide.

In the case of solutions, creating the gelatins, besides the carbamide influence on the water, carbamide molecules act on polymoleculae, destroying the helium communications. It all should be lead to worth of gelatin and decrease of parameters, characterising the gelatincreating systems, that is proved in ref [9,10], where reological investigations, carried out with the water solutions of agara and agarosa at urea concentrations from 1 till 10 moles, show the strong carbamide influence on the gelatin creation processes in these solutions. The results of the given paper prove this. The values D , t_{gel} , t_{mel} and R with the carbamide addition (fig.2,4-6 and tables), i.e. with the increase of activity, i.e/ the solving capability of solvent (water) strongly decrease, that is proved about weak of points of the space grid of gelatin and destruction of gelatin itself. It is possible, that the influence of intermolecular and helium communications decreases, that leads to the decrease of the intensity of gelatins in urea presence. This also proves the decreases about creation of less intensive gelatins at the addition of carbamide.

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AQAROZA-SU-KARBAMİD SİSTEMİNDƏ GELƏMƏLƏGƏLMƏ PROSESİNİN TƏDQIQI

İşdə optik sıxlığın dispersiyası metodu ilə karbamidin aqarozanın sulu məhlullarında geləmələgəlmə prosesinə təsiri öyrənilmişdir. Məhlulların soyudulması və qızdırılması prosesində optik sıxlığın temperatur asılılığı alınmışdır. Məhlulların geləmələgəlmə və ərimə temperaturları, moleküllü hissəciklərin konsentrasiyası və ölçüləri təyin olunmuşdur. Müəyyən olunmuşdur ki, karbamid geləmələgəlmə prosesini ləngidir və onların temperaturun kiçik qiymətləri istiqamətində sürüşdürür. Karbamid molekullararası hidrogen rabitələrini qırır və bununla da gəlin möhkəmliyini azaldır.

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ИССЛЕДОВАНИЕ ПРОЦЕССОВ СТУДНЕОБРАЗОВАНИЯ В СИСТЕМЕ АГАРОЗА-ВОДА-КАРБАМИД

В данной работе изучено влияние карбамида на процесс студнеобразования, на структурирование в водных растворах агарозы с использованием метода дисперсии оптической плотности. Получены температурные зависимости оптической плотности при охлаждении растворов и нагревании студней. Определены температуры студнеобразования и плавления, размеры и числовая концентрация (число частиц в единице объема) надмолекулярных частиц. Установлено, что карбамид тормозит процесс студнеобразования, сдвигая температуры плавления и начала студнеобразования в область более низких значений. Карбамид, разрушая межмолекулярные и водородные связи, разрушая структуру воды, ослабляет прочность студней.

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