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SWELLING OF POLYACRYLAMIDE GEL FROM SOLUTIONS OF VARIOUS SALTS

Annotation

In this work, a polyacrylamide gel with 2% cross-links was synthesized and its swelling properties in $NaHCO_3$, NaCl and $CaCl_2$ solutions were studied using the optical micrometry method. The results of the study showed that the swelling degree of the gel depends on the nature and concentration of the electrolytes. It was found that the swelling degree increases in solutions of sodium salts, and decreases in solutions of calcium chloride. The results obtained indicate the possibilities of using PAAm gel as a sensor and sorbent material.

Keywords: polyacrylamide gel, optical micrometry, swelling process, electrolyte solutions, NaCl, $CaCl_2$, $NaHCO_3$, hydrogel, sensor materials, polymer sorbents.

НАБУХАНИЕ ГЕЛЯ ПОЛИАКРИЛАМИДА ИЗ РАСТВОРОВ РАЗЛИЧНЫХ СОЛЕЙ

Аннотация

В данной работе был синтезирован полиакриламидный гель с 2% сшивок, и с помощью метода оптической микрометрии были изучены его свойства набухания в растворах $NaHCO_3$, NaCl и $CaCl_2$. Результаты исследования показали, что степень набухания геля зависит от природы и концентрации электролитов. Было установлено, что степень набухания увеличивается в растворах солей натрия и уменьшается в растворах хлорида кальция. Полученные результаты указывают на возможность использования полиакриламидного геля в качестве сенсорного и сорбентного материала.

Ключевые слова: Полиакриламидный гель, оптическая микрометрия, процесс набухания, электролитные растворы, NaCl, $CaCl_2$, $NaHCO_3$, гидрогель, сенсорные материалы, полимерные сорбенты.

TURLI TUZLAR ERITMALARIDAN POLIAKRILAMID GELINING BO‘KISHI

Annotatsiya

Mazkur ishda tarkibida 2% ko‘ndalang bog‘lar tutgan poliakrilamid geli sintez qilinib, uning $NaHCO_3$, NaCl va $CaCl_2$ eritmalarida bo‘kish xossalari optik mikrometriya usuli yordamida o‘rganildi. Tadqiqot natijalari gelning bo‘kish darajasi elektrolitlarning tabiati va konsentratsiyasiga bog‘liq ekanligini ko‘rsatdi. Natriy tuzlari eritmalarida bo‘kish darajasi ortishi, kalsiy xlorid eritmalarida esa kamayishi aniqlandi. Olingan natijalar PAAm gelidan sensor va sorbent material sifatida foydalanish imkoniyatlarini ko‘rsatadi.

Kalit so‘zlar: poliakrilamid geli, optik mikrometriya, bo‘kish jarayoni, elektrolit eritmalari, NaCl, $CaCl_2$, $NaHCO_3$, gidrogel, sensor materiallar, polimer sorbentlar.

Introduction. Nowadays, the use of high molecular polymers is of great importance in many fields such as oil extraction, water treatment, agriculture, paper industry, and biotechnology. Polyacrylamide (PAAm) is one of such polymers, which is distinguished from other polymers by its good water solubility, chemical and mechanical stability, and high flocculation properties [1]. There are anionic, cationic, and nonionic types of polyacrylamide, which are widely used in wastewater treatment, sedimentation of suspensions, and also in increasing the efficiency of various technological processes [2]. Polyacrylamide is obtained as a result of free radical polymerization of acrylamide monomer. Initiators such as potassium persulfate, ammonium persulfate, and hydrogen peroxide are used in this process [3]. The molecular weight and physicochemical properties of the synthesized polymer are also significantly affected by polymerization conditions such as monomer concentration, reaction medium, temperature, and initiator amount [4]. Therefore, improving polyacrylamide synthesis processes and improving product quality is one of the current pressing issues. Currently, much scientific work is being carried out on the development of polyacrylamide-based hydrogels, interpenetrated polymer networks (IPNs) and highly branched polymers. Such materials are considered to have unique properties such as pH sensitivity, large water absorption and adsorption of heavy metal ions and dyes, and are currently considered important materials for solving many environmental problems [5,6]. In particular, polyacrylamide/polyacrylate-based hydrogels are widely used in water treatment technologies due to their high saturation and adsorption properties [5]. In addition, partially hydrolyzed polyacrylamides, which have high molecular weight and good water solubility, are widely used in the oil production industry to increase oil recovery [7]. Modern research is aimed at in-depth study of the thermal stability, rheological properties and polymerization kinetics of polyacrylamide, which further expands its potential for creating new functional materials [8,9]. Based on this, the synthesis of polymer gels based on polyacrylamide in laboratory conditions, as well as the study of the mechanism of the synthesis process and the study of the physicochemical properties of the obtained polymer gel are of great scientific and practical importance. The aim of this work is to analyze the process of obtaining polyacrylamide gel as a result of free radical polymerization of acrylamide monomer and to determine the possibility of using the obtained product as a sensitive sensor in studying the processes of precipitation of polymer gels from aqueous solutions of various salts.

Methodological part: The process of PAAm gel precipitation from aqueous solutions of various salts was studied using the optical micrometry method (OMU). The optical micrometry method is dedicated to studying the process of precipitation of polymer gels from solutions of various electrolytes or from a specific solvent. The thermodynamic approach [10] and kinetic [11] laws are used to analyze the results obtained in OMU experiments. The essence of OMU, its working principle, and mathematical algorithm are presented elsewhere [12], and the device structurediagram is presented in Figure 1.

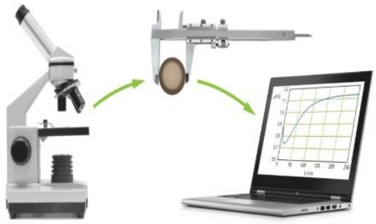

Figure 1. Equipment for determining the process of PAAm gel dissolution from aqueous solutions by optical micrometry: 1 – optical microscope equipped with a video camera, 2 – personal computer with a software package

This method is carried out in the following sequence: PAAm gel dissolved in water is placed in a cell and the gel granules are photographed through a microscope. Then the gel granules are transferred to another cell filled with the solution being determined, and the cell is covered with glass and placed on the microscope stage. After that, the gel dissolution process is photographed through a video camera at certain intervals. The volume of the gel in the initial image is assumed to be equal to one, and the change in the volume of the granules in all other images is calculated using the following equation.

$$V_{nib.} = V_i / V_0 \qquad (1)$$

Here, $V_{nib.}$- change in the relative volume of PAAm gel granules, V_0- volume of gel granules dissolved in water, V_i – volume of granules in a solution of i-concentration.

In a similar sequence, experiments are carried out with solutions of different concentrations of a certain electrolyte and the gel dissolution process is determined. Based on the results obtained, kinetic curves of the time dependence of the relative volume change of granules during their stay in solution are constructed.

Experimental part. To synthesize a polyacrylamide (PAAm) gel with 2% cross-links, 20 g of acrylamide as a monomer, 1.34 g of N,N-methylbisacrylamide as a cross-linking agent, and 0.64 g of ammonium persulfate as an initiator were dissolved in 76 ml of distilled water in a 200 ml chemical beaker. After complete dissolution, the mixture was cooled in an ice bath. Subsequently, 0.6 g of potassium sulfite was dissolved in 4 ml of water to prepare an activator solution for the radical polymerization reaction. Using the same method, a PAAm with 2% cross-links was obtained using a solution diluted twice. Twice as much water was used for this process. The gel granules obtained as a result of the synthesis were spherical in shape, with diameters ranging from 0.2 to 0.9 mm. The following reagents were used in the experiments: $NaHCO_3$, NaCl, $CaCl_2$, 0.1N hydrochloric acid, EDTA (Trilon-B) fixed solutions, methyl orange, murexide, eriochrome black indicators. Sodium ions were determined by flame photometry, calcium ions by complexometric methods.

Analysis of the obtained results. The process of swelling of PAAm gel with 2% cross-links synthesized using OMU from solutions of salts with different concentrations such as $NaHCO_3$, NaCl and $CaCl_2$ was studied. The obtained results are presented in Table 1 and Figure 2.

Table-1. Dependence of PAAm gel saturation degree on equilibrium solution concentration

No	1	2	3	4	5	6	7	8	9	10
C_N	0	0,1	0,2	0,3	0,4	0,5	0,6	0,8	0,9	1,0
V/V_0 $NaHCO_3$	1,0	1,168	1,134	1,065	1,042	1,014	0,956	0,953	0,951	0,959
V/V_0 NaCl	1.0	1,274	1,158	1,088	1,054	1,032	1.002	0,973	0,964	0,960
V/V_0 $CaCl_2$	1,0	0,948	0,912	0,896	0,873	0,850	0,845	0,841	0,838	0,836

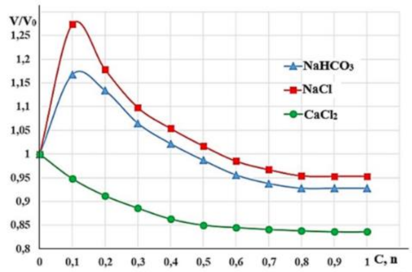

Figure 2. Dependence of the degree of swelling of PAAm-2% gel on the nature and concentration of salts in the equilibrium solution

The results obtained in the experiments show that the relative change in the degree of swelling of PAAm-2% gel significantly depends on the nature and concentration of salts in the equilibrium solution (Figure 3).

It can be seen from the figure that during the swelling process from sodium salt solutions, the gel volume increases significantly at low concentrations (up to 0.2 g/l), then decreases uniformly with an increase in the concentration of the external solution at equilibrium, i.e., the swelling process passes through an extremum. The decrease in the swelling process is evidenced by a decrease in the solvent activity in the solution. On the contrary, during the swelling of the gel from CaCl2 solutions, a decrease in the relative volume was observed in the range of concentrations studied. This result is explained as follows: the hydrogen bonds between the functional groups in the PAAm gel are broken under the influence of sodium ions, and an increase in the volume of the gel is observed (Figure 3).

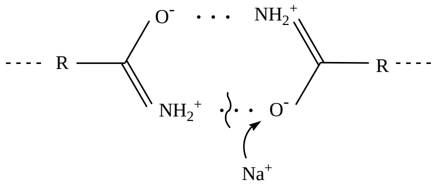

Figure 3. Cleavage of hydrogen bonds between functional groups in PAAm under the influence of sodium ions

Unlike the sodium cation, the divalent calcium cation forms additional three-dimensional crosslinks due to the coordination of the amide groups in the gel with oxygen atoms. As a result, the relative size of the PAAm gel decreases with the increase in the concentration of $CaCl_2$ solution (Fig. 4).

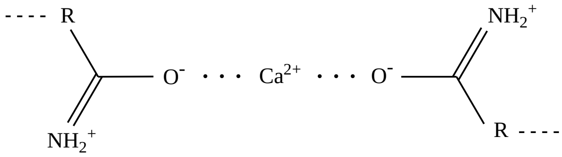

Figure 4. Effect of calcium cations on PAAm functional groups

The kinetics of PAAm gel dissolution from various salt solutions were studied using salt concentrations of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0 n. PAAm granules dissolved in water were placed in salt solutions of certain concentrations and held for a certain time until equilibrium was established, and the relative volume change of the gel was determined using the optical micrometric method. The results obtained for NaCl solutions are presented in Figure 5 and Table 2.

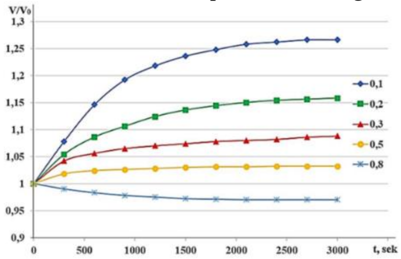

Figure 5. Time dependence of PAAm gel swelling from NaCl solutions of different concentrations

Table-2. Time dependence of PAAm gelation degree in NaCl solutions of different concentrations

C_N	No	1	2	3	4	5	6	7	8	9	10
0,1	V/Vo	1,000	1,078	1,146	1,192	1,218	1,236	1,248	1,258	1,262	1,266
0,2	V/Vo	1,000	1,054	1,086	1,106	1,124	1,136	1,144	1,150	1,154	1,156
0,3	V/Vo	1,000	1,042	1,056	1,065	1,070	1,074	1,078	1,080	1,082	1,086
0,5	V/Vo	1,000	1,018	1,024	1,026	1,028	1,030	1,031	1,031	1,032	1,032
0,8	V/Vo	1,000	0,990	0,983	0,978	0,975	0,972	0,971	0,970	0,970	0,970
	t, s	0	300	600	900	1200	1500	1800	2100	2400	2700

Using the kinetic curve values obtained in the experiments, three-dimensional (3D) surface area plot plots were constructed for solutions of different salt concentrations using the “Polymer_swelling_kinetics 5.1” software. As an example, the result obtained for NaCl salts is shown in Figure 6.

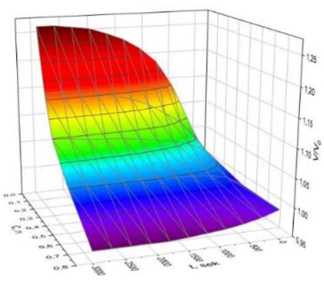

Figure 6. 3D surface view of the PAAm gelation process from NaCl solutions of different concentrations

The surface areas presented in Figure 6 allow us to find the concentration of the solution being determined.

Conclusion. The results obtained in the experiments showed that the degree of saturation of PAAm gel from solutions of various salts, unlike other polymer sorbents and gels, varies significantly depending on the concentration and nature of the salts (up to 0.2 g/l at low concentrations). This effect occurs due to the disruption of hydrogen bonds between functional groups in different parts of the polymer chain in the polyacrylamide structure. The decrease in the degree of saturation of PAAm gel with increasing equilibrium solution concentration is explained by a decrease in the number of water molecules in the polymer solution phase in all studied systems. In addition, it was shown that the degree of saturation of PAAm gel is more sensitive to the nature of cations than to the nature of anions. This conclusion allows using PAAm gel for the analysis of solutions with mixed composition.

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