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# ILMIY AXBOROTNOMA

## НАУЧНЫЙ ВЕСТНИК
## SCIENTIFIC JOURNAL

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# STUDY OF THE KINETICS OF PVA SWELLING FROM SOLUTIONS OF STRONG ELECTROLYTES CONTAINING MIXED SOLVENTS

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**Abstract.** The effect of a mixed solvent of water - isopropanol was studied on the relative volume of polyvinyl alcohol gel in solutions of various electrolytes of different concentrations. Kinetic curves of the change in the degree of swelling of PVA in solutions of LiCl, NaCl, KCl, NaBr, NaI, $Na_2SO_4$ , HCl, $HNO_3$ are given. The effect of a mixed solvent on the sensitivity of determining the concentrations of the proposed compounds is shown.

**Keywords:** cross-linked polyvinyl alcohol, swelling, mixed solvents, electrolyte solution, concentration, amount of substance

## Tarkibida aralvan erituvchilar bo‘lgan kuchli elektrolitlar eritmalaridan PVS bo‘kish kinetikasini o‘rganish

**Annotatsiya.** Aralash suv-izopropanol erituvchili turli konsentratsiyali har xil elektrolitlar eritmalarining polivinil spirt geli bo’kish darajasiga ta'siri o'rganildi. LiCl, NaCl, KCl, NaBr, NaI, $Na_2SO_4$, HCl, $HNO_3$ eritmalarida PVS ning bo’kish darajasi o‘zgarishining kinetik egri chiziqlari keltirilgan. Taklif etilayotgan birikmalar kontsentratsiyalarini aniqlashning sezgirligiga aralash erituvchining ta'siri ko'rsatilgan.

**Kalit so‘zlar:** ko‘ndalang bog‘langan polivinil spirt, bo‘kish, aralash erituvchilar, elektrolit eritmasi, konsentratsiya, moddaning miqdori.

## Исследование кинетики набухания ПВС из растворов сильных электролитов содержащих смешанных растворителей

**Аннотация.** Исследовано влияние смешанного растворителя вода - изопропанол на относительный объём геля поливинилового спирта в растворах различных электролитов разной концентрации. Приведены кинетические кривые изменения степени набухания ПВС в растворах LiCl, NaCl, KCl, NaBr, NaI, $Na_2SO_4$, HCl, $HNO_3$. Показано влияние смешанного растворителя на чувствительность определения концентраций предложенных соединений.

**Ключевые слова:** сшитый поливиниловый спирт, набухание, смешанные растворители, раствор электролита, концентрация, количество вещества

**Introduction.** Polyvinyl alcohol (PVA), a versatile hydrophilic polymer gel, has attracted considerable attention in various branches of the chemical industry due to its chemical stability and mechanical properties. The influence of the density of aqueous-organic solvents on the swelling of polyvinyl alcohol gel is presented in [1, 2]. The authors of [3-5] showed the use of composites obtained from PVA gel in tissue engineering. In addition, [6] an effective application of PVA gel for

the creation of environmentally friendly composite sheets with improved mechanical properties is presented. This approach not only promotes waste management, but also expands the use of PVA in green technologies. To date, a special place is occupied by the study of the physicochemical properties of PVA gel from solutions containing mixed solvents. The paper [7] presents the swelling kinetics of PVA from solutions of low-molecular substances containing mixed water-alcohol solvents, in which the volume fraction of alcohol is 65%. In [8, 9] the thermodynamic properties of the phases of water-alcohol and salt systems are given in detail. According to the results obtained, they proved that an increase in the amount of electrolytes in the mixture leads to an increase in the separation coefficient of the components of the separated mixtures, and also increases the selectivity of the gel.

**Theoretical part.** Mixtures of solvents, called mixed solvents, often have a higher dissolving power than each of their components separately. This phenomenon is known as co-dissolution, and the individual components of the mixture are co-solvents [10]. The use of mixed solvents makes it possible to achieve virtually any desired properties of a liquid medium, which facilitates many physicochemical and chemical processes. Among them, water-alcohol mixed solvents are of particular interest. It is known that due to the presence of hydrogen bonds, water is considered an associated liquid. A hydrogen bond is formed between a hydrogen atom covalently bonded to an electronegative oxygen atom of one water molecule and an oxygen atom of another molecule. The energy of a hydrogen bond is 30 kJ/mol, and this energy is significantly weaker than covalent bonds. Consequently, the associates of such waters that form disintegrate and form again in other structures. In addition, alcohols also belong to associated liquids. Thus, water-alcohol solutions are mixed associates. The structure of such associates cannot be considered sufficiently studied at present.

It is known that a significant portion of water retains a tetrahedral structure. Isopropyl alcohol molecules, which have a larger size, when integrated into the structure of water break it apart, whereas the inclusion of water molecules in the structure of alcohol does not lead to significant changes in the latter. When tiny amounts of isopropyl alcohol are dissolved, the structure of water is preserved, experiencing minor deformations. With an increase in the concentration of isopropyl alcohol, the structure of water is destroyed. When medium concentrations of isopropyl alcohol are reached in the mixture, an equilibrium is achieved between associates of heterogeneous molecules, aggregates of identical molecules, and single molecules of water and isopropyl alcohol. This phenomenon leads to a constant composition of the mixed solution. Consequently, such solutions have the greatest microheterogeneity. At high concentrations of isopropyl alcohol, alcohol with absorbed water molecules dominates in the mixture [11]. This concept shows the existence of three concentration regions of water-alcohol mixed solvents. Firstly, water with alcohol molecules in free cavities, secondly, the transition structure of water-alcohol mixed solvents and thirdly, the structure of alcohol with individual water molecules applied. From the above , in mixed (water-alcohol) solutions, water and alcohol molecules interact, forming hydrated complexes, that is, structures in which water molecules cover alcohol molecules (or vice versa). The composition of these complexes, as well as the structure of the solution, depend on the ratio of water and alcohol concentrations [12]. Water-alcohol mixtures are quite often used, for example, in reversed -phase high-performance liquid and thin-layer chromatography to increase the eluting power of the solvent [13]. Different substances have different effects on the eluting power of the solvent, and therefore on the degree of swelling of polymer gels. Based on the above, this article presents the results of the swelling kinetics of PVA in solutions containing mixed solvents “water – isopropanol”.

**Experimental part.** The study of the swelling kinetics of the hydrophilic polymer sorbent in solutions with mixed solvents was carried out by the optical micrometry method (MOM). The setup on which the experiments were carried out is shown in Fig. 1. The experiments used solutions of LiCl, NaCl, KCl, $NH_4Cl$ with mixed solvents of water and alcohol. The volume fraction of isopropanol in the mixture was 60%. In these solutions, the concentration was achieved from 0.1 N to 1.0 N. Spherical PVA granules with diameters of 0.35-1.15 mm were used as a sensor. The specific values of polyvinyl alcohol gel are given in Table 1. Cross-linked PVA granules were synthesized in an alkaline medium according to the scheme below:

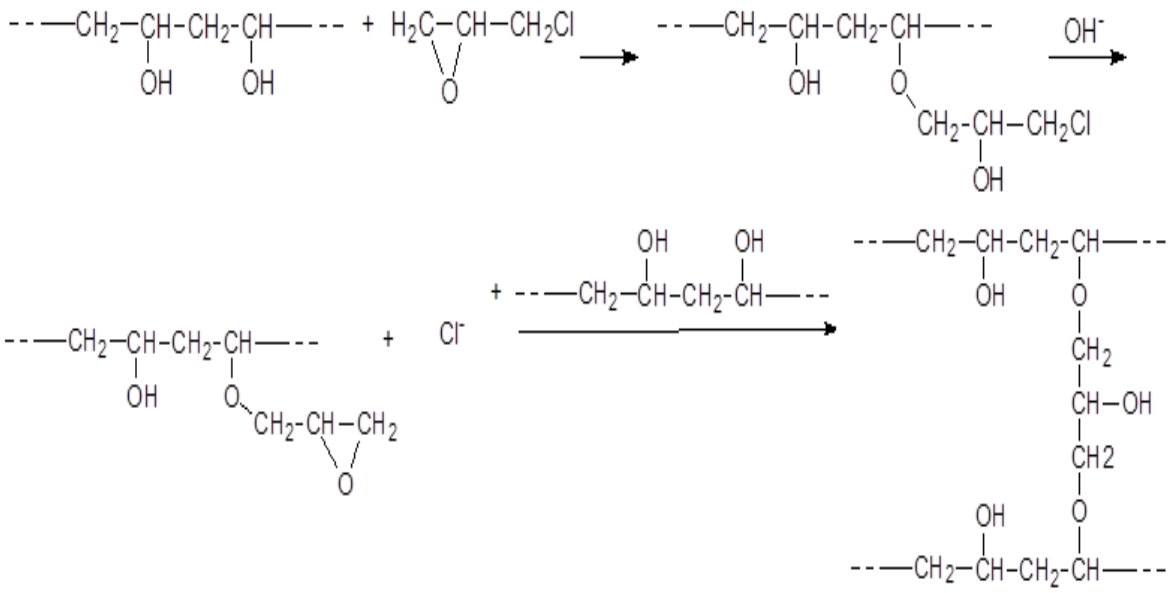


Table -1

Specific values of cross-linked polyvinyl alcohol gel

| Name of polymer gel | Average molecular weight , kg/mol | Density, ρ, g/ $cm^3$ | $E_v$, mg- eq /ml | $E_m$, mg- eq /g |
|---|---|---|---|---|
| PVS-20 | 65 | 1,277 | 18.9 | 14.8 |

where: ρ – polymer density, $E_m$ – capacity of the polymer gel by mass, $E_v$ – capacity of the polymer gel by volume, M – average molecular mass of the polymer chain.

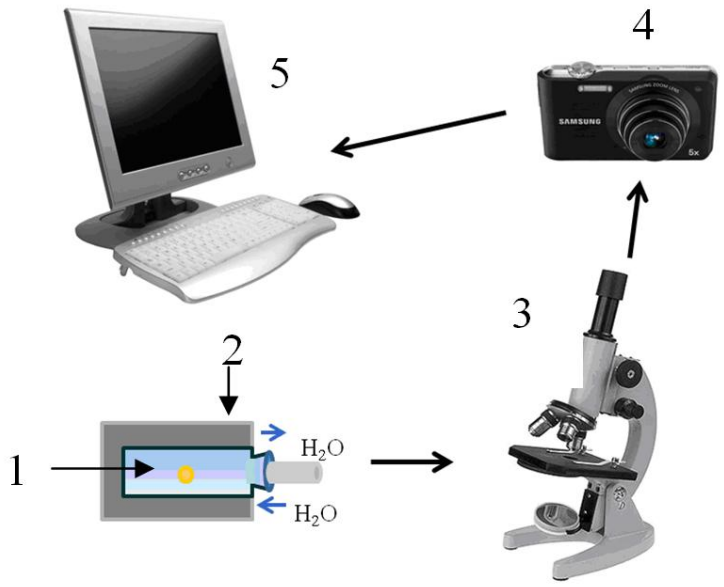



**Figure 1**. Installation of the optical micrometry device. 1 – quartz cuvette, 2 – cell, 3 – microscope, 4 – video camera, 5 – personal computer.

**Discussion of results**. All results were obtained based on the heterophase model of the structure of a swollen hydrophilic polymer [14]. In this model, the hydrophilic polymer is considered as a heterophase. Such a system consists of a polymer solution and an external solution. A detailed description of this model is given in [15-17]. During the experiments, the dependences of the change

in the relative volume of the PVA gel on the concentration of the external solution were obtained for both aqueous and of these salts with mixed water-alcohol solvents. The data obtained in the experiments are shown in Fig. 2 a) and 2 b. And also in Table 2.

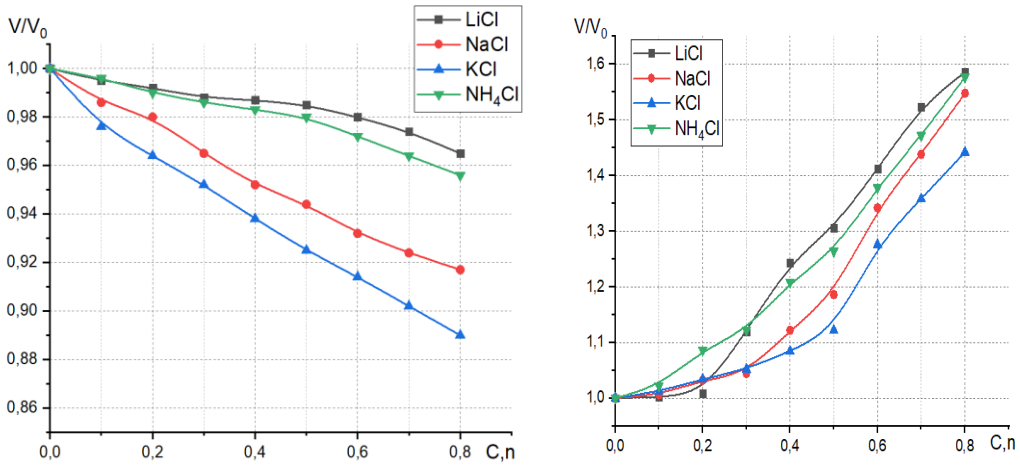



**Figure 2**.a, b. Dependences of the change in the relative volume of PVA gel on the concentration of the external solution. a) from aqueous solutions, b) from solutions with mixed solvents water-alcohol.

Table-2

Experimental data on the kinetics of PVA swelling from salt solutions.

| C,n | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
|---|---|---|---|---|---|---|---|---|
| LiCl | | | | | | | | |
| $V/V_0$ ($H_2O$) | 0.995 | 0.992 | 0.988 | 0.987 | 0.985 | 0.980 | 0.974 | 0.965 |
| $V/V_0$ ($H_2O$ - alcohol) | 1.002 | 1.008 | 1.122 | 1.244 | 1.306 | 1.412 | 1.524 | 1.586 |
| NaCl | | | | | | | | |
| $V/V_0$ ($H_2O$) | 0.986 | 0.980 | 0.965 | 0.952 | 0.944 | 0.932 | 0.924 | 0.917 |
| $V/V_0$ ($H_2O$ - alcohol) | 1.000 | 1.032 | 1.044 | 1.122 | 1.186 | 1.342 | 1.438 | 1.548 |
| KCl | | | | | | | | |
| $V/V_0$ ($H_2O$) | 0.976 | 0.964 | 0.952 | 0.938 | 0.925 | 0.914 | 0.902 | 0,890 |
| $V/V_0$ ($H_2O$ - alcohol) | 1.012 | 1.034 | 1.052 | 1.084 | 1.122 | 1.276 | 1.358 | 1.442 |
| NH4Cl | | | | | | | | |
| $V/V_0$ ($H_2O$) | 0.996 | 0.990 | 0.986 | 0.983 | 0.980 | 0.972 | 0.964 | 0.956 |
| $V/V_0$ ($H_2O$ - alcohol) | 1.022 | 1.086 | 1.122 | 1.208 | 1.264 | 1.378 | 1.472 | 1.577 |

Figure 2 shows that in solutions of lithium, sodium, potassium and ammonium chlorides, in the composition of mixed solvents, it was observed that with an increase in the concentration of salts,

the relative volume of the PVA gel increases, and in aqueous solutions it decreases. In these mixed solutions, the volume fraction of isopropyl alcohol is 60%.

The change in the swelling degree of the gel in the studied concentration range in the mixed solution turned out to be more significant than in aqueous solutions. In solutions of chlorides of cations of the first group, the swelling degree noticeably decreases from lithium to potassium in aqueous solutions, and increases in solutions with mixed solvents. This experimentally obtained result confirms the hydration of alkali metal ions (Fig. 3).

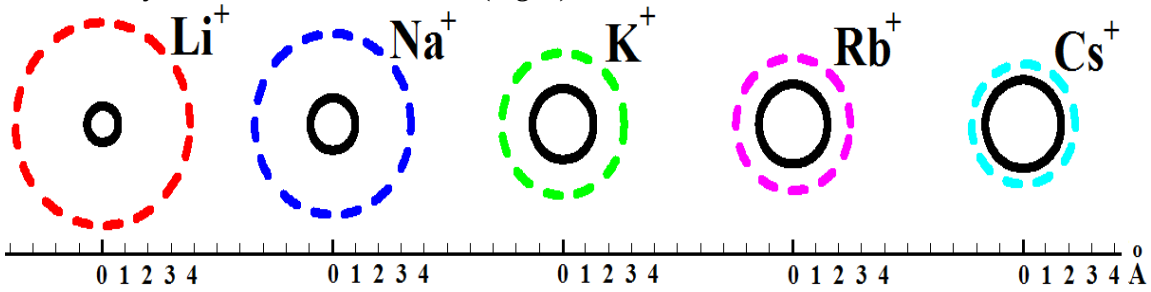



**Figure 3.** Hydration of alkali metal ions [18].

Based on the experimental data for each studied substance, a 3D surface was constructed, reflecting the dependence of the relative volume of the polymer gel on time and concentration of the studied solution. Using such a surface, it is possible to determine the concentration of the studied component at any time, supplying it with experimentally obtained data showing the dependence of the degree of swelling of the gel $V / V_0$ on time $t$. As an example, Figure 4 shows a 3D surface of the swelling kinetics of PVA gel in LiCl solutions of various concentrations.

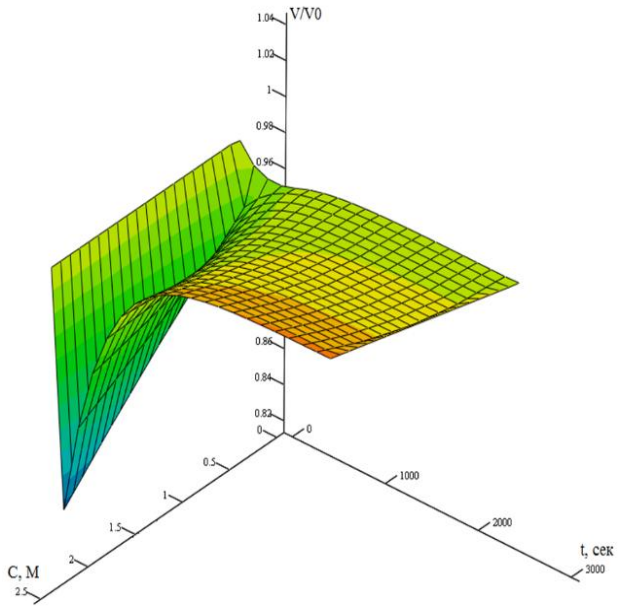



**Figure 4.** 3 D - surface of the kinetics of swelling of PVA gel in LiCl solutions in the concentration range from 0.1 N to 1.5N.

**Conclusion.** The swelling kinetics of PVA granules in aqueous and aqueous-alcoholic solutions of LiCl, NaCl, KCl, $NH_4$ Cl was studied using optical micrometry. It was found that this method has a significantly higher sensitivity when using a mixed solvent of water- isopropanol with a volume fraction of isopropanol of 60%, compared to pure water as a solvent. In addition, it was found that the decrease in the sensitivity of the optical method with a decrease in the concentration of the studied solutions is explained by the fact that the amount of water sorbed by the hydrophilic groups of the polymer gel changes. It is shown that the addition of an organic solvent reduces the amount of sorbed mixed solvent, lowers the activity of water and increases the sensitivity of the method.

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