

## INVESTIGATION OF THE MECHANISM OF SELECTIVE EXTRACTION OF IONS OF VARIOUS SALTS FROM WATER, USING POLYAMIDE MEMBRANES

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**Abstract.** *Introduction.* The processes of membrane separation and concentration belong to the category of critical technologies for obtaining and processing the structural and functional materials for water desalination. The supply of softened water to the reverse osmosis devices practically does not solve the problem of membrane contamination with salt ions. The material, of which the membrane is made, has a high affinity for the solvent (mainly water), and a low affinity for the dissolved component. The selected objects and the subject of research - the diffusion of water salts on the surface of polyamide (PA) - allow us to count on a possibility of confident membrane separation of the components of the aqueous solutions. The prospects and advantages of polyamides membranes are determined on the basis of the analysis of the kinetics of membrane separation, the polyamides membrane is resistant to the studied salt solutions. *The purpose* of this work is to study the features and regularities of the mechanism of selective extraction of salt ions from water by polyamide membranes. The methods of water purification are of great importance in the selective extraction of salt ions from water, using polyamide membranes. *Methodology.* Polyamides have a high selectivity with respect to salts, but the flow of water through them is slightly lower. At the pH range of polyamides of 2.0 – 10, they withstand processing temperatures up to 100°C without significant changes in the porous structure, allow a multiple regeneration, and are resistant to most acids, depending on the pH of the medium. *Results.* According to the results of the pilot tests in the extraction of salt ions from water, using polyamide membranes, it has been found that in the pH range of 6-7, the joint presence of the main charged forms of salt ions is assumed. To prevent precipitation of larger forms, it is necessary to work with the solutions, diluted by ions in the presence of the background electrolytes. *Conclusion.* Thus, based on the results, it follows that the values of the diffusion coefficients of salt ions in the membranes with the pore radii from 5 to 8 nm at pH of 6.5–7.5 are generally comparable to salt ions. The revealed features of the diffusion of salt ions in the PA membranes (the exponential dependence of the diffusion coefficient on the pore radius of membranes, the pH value) and comparison of the obtained data with the available salts, make it possible to determine the prospects and conditions for their separation in the PA membranes.

**Key words:** diffusion, membranes, salt ions, polyamides, water purification

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## 1. Introduction

The processes of membrane separation and concentration belong to the category of critical technologies for obtaining and processing the structural and functional materials for water desalination. The supply of softened water to the reverse osmosis devices practically does not solve the problem of contamination of membranes with salt ions. The material, of which the membrane is made, should have a high affinity for the solvent (mainly water) and a low affinity for the dissolved component. The selected objects and the subject of the study - the diffusion of water salts on the surface of polyamide (PA) - allow us to count on the possibility of confident membrane separation of the components of the aqueous solutions.

The prospects and advantages of the PA membranes are determined on the basis of the analysis of the kinetics of membrane separation, the PA membrane is resistant to the studied salt solutions [1-2]. The calculation of the selectivity characteristics of membrane desalination, on the basis of the fundamental physicochemical characteristics of the solution, permeate, is a difficult task due to a large number of the influencing factors [3].

The purpose of this work is to study the features and regularities of the mechanism of selective extraction of salt ions from water by polyamide membranes. The methods of water purification are of great importance in the selective extraction of salt ions from water, using polyamide membranes.

## 2. Experimental part

Polyamide has a high selectivity with respect to salts, but the flow of water through them is slightly lower. At the pH range (cleaning pH) of 2.0 – 10 (1-12) of PA, they withstand the processing temperatures up to 100<sup>0</sup> C without significant changes in the porous structure, allow multiple regeneration, and are resistant to most acids, depending on the pH of the medium. The PA membrane has a sufficiently large thickness of up to 150 microns. Such thick membrane films lead to a sharp decrease in the mass transfer rate. However, this effect is compensated by an extremely high membrane surface per volume unit: the specific surface area reaches 30,000 m<sup>2</sup>/m<sup>3</sup> [4,7-8].

It was found [1-3,10] that the diffusion mobility of ions in the PA membranes is generally lower than in the free solutions, even in the region of significant pore radii. A decrease in the pore size leads to a decrease in the

diffusion coefficients, associated with the difficulty of moving ions in the wall layers of the solution. At the same time, the difference in the properties of the boundary layers from the properties of the bulk solutions is associated with the structuring of water on the polymer surface [1-3,10,13-14]. The orienting action of the polymer surface of the OH groups leads to the rearrangement and ordering of the intermolecular hydrogen bond grid of the wall water, to the restriction of the molecular mobility, to an increase in the viscosity of the boundary layers [12; 14], to a decrease in the solvent capacity and dielectric permittivity of water in the small-radius pores [13].

Determination of the porosity or free volume of the membrane material is one of the most important factors, determining the kinetics of the membrane processes [3-5]. Thus, the determination of the internal diffusion coefficient in the membrane directly depends on this characteristic [3, 12].

If we assume that the entire free volume of the polymer membrane is evenly distributed over all the structural fragments, which make up the membrane substance, we can introduce the concept of free volume per fragment (Figure 1).

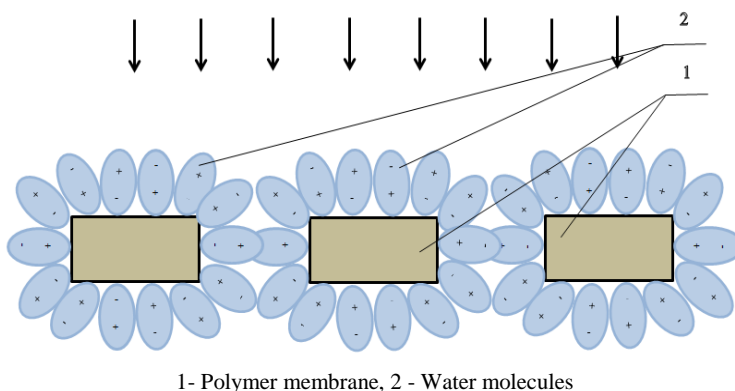
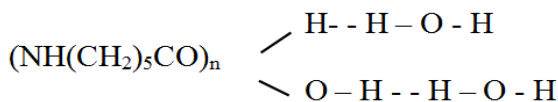


Figure 1- Location of the molecules of water on the membrane surface

There is hydrogen at the surface of the PA membranes, when in contact with water, a hydrogen ion is formed:



For the polymer membranes, whose macromolecules are constructed from the alternating fragments with a certain mobility, the free volume can be defined as the sum of the free volumes per each fragment of the structure:

$$\bar{V}_f = \sum_i N_i V_{if}$$

where  $N_i$  is the number of particles per volume unit.

The formula can also be written as [3]:

$$\bar{V}_f = \sum_i \varphi_i V_{if},$$

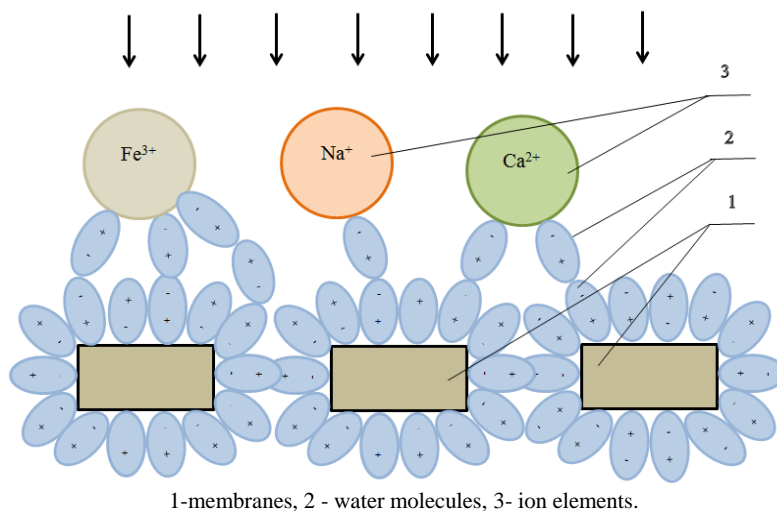
where  $\varphi_i$  is the volume fraction of the fragments of macromolecules, which make up the membrane in its matrix.

The specific free volume, determined in this way per a structural fragment, depends on the temperature, pressure and chemical nature of both the polymer substance of the membrane itself and the nature of the substance diffusing in it. When describing the effect of the molecular weight of the membrane substance on the diffusion properties of the matrix, which determines the structure of the membrane, the issues of the formation of the internal structure in the contact zones of macromolecules on the inner and end sections of the polymer chains should be separated.

It is known that there are two main ways of organizing macromolecules in the polymer matrix of the membrane [3, 6-11]. In the first case, the ends of a polymer chains are free, whereas in the second case, they are “stitched”.

Consider a case of free ends of the polymer chains in the matrix. As follows from the statistical physics, in this case, the thermal motion of the free end fragments of the polymer chains of the membrane matrix can be considered as performing thermal motion in relative independence from the thermal motion of the main part of the chains.

Suppose that the type of connection of the end fragments with the main part of the chain can be defined as a hydrogen compound with salt ions (Figure 2).



**Figure 2** – The arrangement of the water molecules and ion elements on the membrane surface

### 3. Results and discussion

The efficiency of membrane filtration is determined by comparing the values of the diffusion coefficients of the separated or extracted components of the solutions [9-12]. After substances are dissolved in water, hydrate shells are formed around their particles: ions, molecules, small associates, micelles (large associates), i.e. all particles (with rare exceptions), being charged, tend to attract and orient the dipole water molecules around them, i.e. distort or even destroy the original structure of water.

The degree of manifestation of this tendency depends on the size of the charge and the configuration of the particle. At the same time, a two-layer hydrate shell appears around ions, polar molecules and micelles, consisting of a dense layer of the oriented water molecules and a loose layer of the semi-oriented water molecules. The dense layer of the hydrate shell can be considered to consist of water clusters interconnected by hydrogen bonds, the structure of which is specific depending on the nature of the hydrated particle. This layer is quite strong, strictly ordered under the action of an electric field, and the water molecules in this layer are “frozen”. In the process of electrolysis, it moves along with the ion. An approximate calculation for the solutions with a relatively low concentration (0.1-0.5M) provides the size of the secondary hydrate shell of 1.5-2.0 nm (15-20 Å), which is commensurate with the pore sizes of the semi-permeable PA membranes.

The thickness of the layer is determined by the charge density of the ion (particle), i.e. the ratio of the charge value of the ion (particle) to its diameter. The average lifetime of water molecules in the hydrate shell depends on the nature of the particle, the concentration of solutes and temperature. The boundary condition for the occurrence of such a system (i.e., the concentration of the electrolyte in the solution) is called the boundary of the complete hydration of the aqueous solution (HAS). For different electrolytes, this concentration is in the range from 2.14 to 4.63 mol/l.

After pilot tests at 3-Energoortalyk JSC, the surfaces of the PA membranes have been examined for the content and location of the element composition of the concentrate on a scanning electron microscope (REM) (Figure 3).

## 90 - membrane paper (general microanalysis)

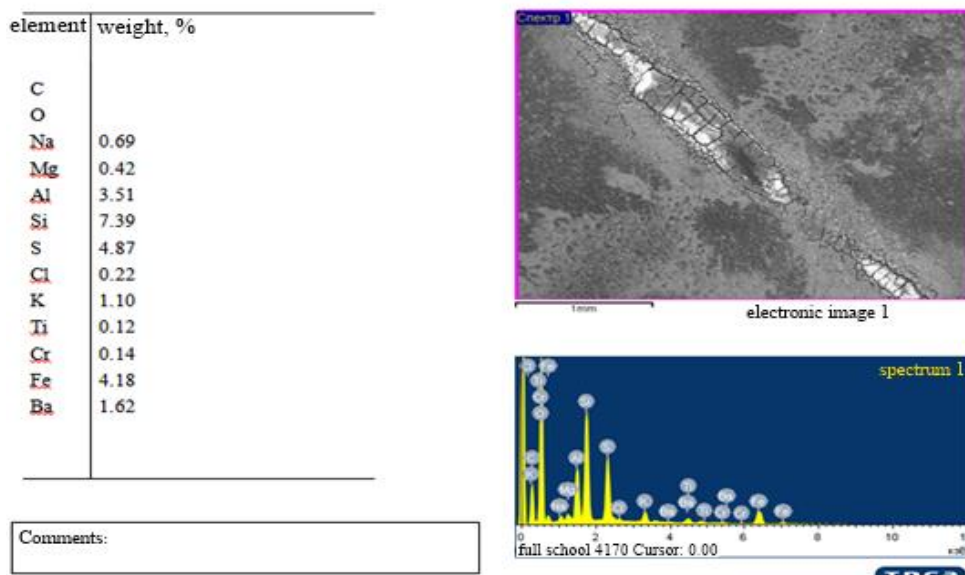
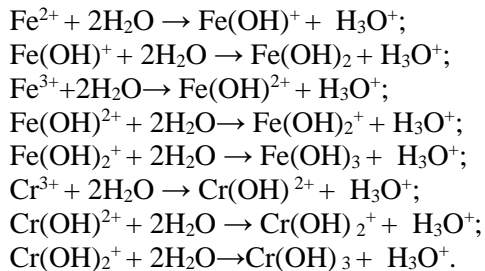
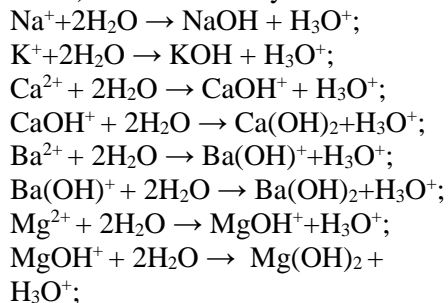


Figure 3 – The content and location of the elemental composition of the concentrate of the surface of the PA membranes

When the salt cations and anions, contained in water, interact, the following reactions occur:

## 1) Cations form hydroxides



## 2) Anions form acids



It is almost impossible to unambiguously establish the form of the existence of particles and their quantitative correlation in the aqueous solutions [5]. In the

pH range of 6-7, the joint presence of the main charged forms of salt ions is assumed. To prevent the precipitation of larger forms, it is necessary to work with the ion-dilute solutions in the presence of the background electrolytes, which, unfortunately, does not meet the conditions of the membrane filtration experiments which we have accepted. In this regard, we have limited ourselves to studying the diffusion of the aqueous solutions of salt ion with pH = 6-7, counting on the manifestation of partial (caused by an increase in  $pH$ ) ion di/trimerization in the mass transfer parameters, which should be accompanied by a decrease in the measured diffusion coefficient.

#### 4. Conclusion

Thus, based on the results of the study of diffusion in membranes, it is possible to consider a possibility of structural transitions in the transported systems.

In this work, the difficulties, connected with the qualitative description and quantitative definition of the parameters of diffusion transport of the solutions of salt ions in the polymer membranes, were solved, taking into account the pore sizes of membranes and the  $pH$  of the solutions.

It should be noted, however, that the values of the diffusion coefficients of salt ions in the membranes with the pore radii from 5 to 8 nm at  $pH = 6.5-7.5$  are generally comparable to salt ions. The revealed features of the diffusion of salt ions in the PA membranes (exponential dependence of the diffusion coefficient on the membrane pore radius,  $pH$  value) and comparison of the data, obtained with the available salts, allow us to determine the prospects and conditions for their separation in the PA membranes.

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#### ПОЛИАМИДТІ МЕМБРАНАЛАРДЫ ҚОЛДАНА ОТЫРЫП, СУДАН ӘРТҮРЛІ ТҮЗДАРДЫҢ ИОНДАРЫН СЕЛЕКТИВТІ АЛУ МЕХАНИЗМІН ЗЕРТТЕУ

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**Түйіндемe.** *Кіріспе.* Мембраналық бөлу және концентрациялық үрдістер суды тұщыландыруға арналған құрылымдық және функционалдық материалдарды өндіру мен өндеудің маңызды технологияларының санатына жатады. Кері осмос құрылғыларына жұмсартылған суды беру тұз иондарымен мембрананың ластану мәселесін іс жүзінде шешпейді. Мембрана жасалған

материалдың еріткішке (негізінен су) жоғары жақындығы және еріген компонентке жақындығы төмен. Таңдалған объектілер мен зерттеу пәні – полиамид (ПБ) бетіндегі су тұздарының диффузиясы – сулы ерітінділердің компоненттерін сенімді мембраналық бөлу мүмкіндігіне сенуге мүмкіндік береді. Полиамидті мембраналардың болашағы мен артықшылықтары мембрананың бөліну кинетикасын талдау негізінде анықталады, полиамид мембранасы зерттелетін тұз ерітінділеріне төзімділікке ие. *Мақсаты*. Бұл жұмыстың мақсаты – полиамидті мембраналар арқылы судан тұз иондарын іріктеп алу механизмінің ерекшеліктері мен заңдылықтарын зерттеу. Полиамидті мембраналар арқылы судан тұз иондарын таңдап алуда суды тазарту әдістерінің маңызы зор. *Методологиясы*. Полиамидтер тұздарға өте селективті, бірақ олар арқылы өтетін су ағыны аздап төмен болады. 2–10 рН диапазонында полиамидтер кеуекті құрылымында айтарлықтай өзгеріссіз 100°C-қа дейінгі өңдеу температурасына төтеп бере алады, бірнеше рет регенерацияға мүмкіндік береді және ортаның рН мәніне байланысты қышқылдардың көпшілігіне төзімді. *Нәтижесі*. Полиамидті мембраналарды қолдану арқылы судан тұз иондарын алуда тәжірибелік сынақтардың нәтижелері бойынша рН = 6-7 аймағында тұз иондарының негізгі зарядталған формаларының бірлескен болуы анықталды. Үлкен формалардың тұнбасын болдырмау үшін фондық электролиттердің қатысуымен иондармен сұйытылған ерітінділермен жұмыс істеу керек. *Қорытынды*. Осылайша, нәтижелерге сүйене отырып, рН = 6,5-7,5 кезінде кеуек радиустары 5-тен 8 нм-ге дейінгі мембраналардағы тұз иондарының диффузиялық коэффициенттерінің мәндері әдетте тұз иондары үшін салыстырмалы болады. ПА мембраналарындағы тұз иондарының диффузиясының анықталған ерекшеліктері (диффузия коэффициентінің мембраналардың кеуекті радиусына, рН мәніне экспоненциалды тәуелділігі) және алынған мәліметтерді ұсталынған тұздармен салыстыру барысында ПА мембраналарында болашақтағы тиімділігі мен оны қолдану жағдайларды анықтауға зор мүмкіндік береді.

**Түйінді сөздер:** диффузия, мембрана, тұз иондары, полиамидтер, су тазалау

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## ИССЛЕДОВАНИЕ МЕХАНИЗМА СЕЛЕКТИВНОГО ИЗВЛЕЧЕНИЯ ИОНОВ РАЗЛИЧНЫХ СОЛЕЙ ИЗ ВОДЫ С ИСПОЛЬЗОВАНИЕМ ПОЛИАМИДНЫХ МЕМБРАН

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**Резюме. Введение.** Процессы мембранного разделения и концентрирования относятся к разряду критических технологий получения и обработки конструкционных и функциональных материалов для обессоливания воды. Подача на обратноосмотические аппараты умягченной воды практически не решает проблему загрязнения мембран ионами солей. Материал, из которого изготовлена мембрана имеет высокое сродство к растворителю (главным образом к воде) и низкое сродство к растворенному компоненту. Выбранные объекты и предмет исследования - диффузия солей воды на поверхности полиамида (ПА) - позволяют рассчитывать на возможность уверенного мембранного разделения компонентов водных растворов. Перспективы и преимущества полиамидных мембран определяются на основе анализа кинетики мембранного разделения, мембрана из полиамида имеет устойчивость к исследуемым солевым растворам. *Целью* данной



работы является изучение особенностей и закономерностей механизма селективного извлечения ионов солей из воды полиамидными мембранами. Большое значение имеют методы очистки воды при селективном извлечении ионов солей из воды с помощью полиамидных мембран. *Методология.* Полиамиды обладают высокой селективностью по отношению к солям, но поток воды через них немного ниже. При диапазоне pH 2–10 полиамиды выдерживают температуру обработки до 100°C без существенного изменения пористой структуры, допускают многократную регенерацию, устойчивы к действию большинства кислот в зависимости от pH среды. Мембрана из ПА имеют достаточно большую толщину до 150 мкм. Столь толстые пленки мембран приводят к резкому снижению скорости массопереноса. Однако этот эффект компенсируется чрезвычайно высокой поверхностью мембраны в расчете на единицу объема: удельная поверхность достигает 30000 м<sup>2</sup>/м<sup>3</sup>. *Результаты.* По результатам опытно-промышленных испытаний при извлечении ионов солей из воды с использованием полиамидных мембран установлено, что в области pH = 6–7 предполагается совместное присутствие основных заряженных форм ионов солей. Для предотвращения выпадения в осадок более крупных форм необходимо работать с разбавленными по ионам растворами в присутствии фоновых электролитов. *Заключение.* Таким образом, на основании результатов следует, что значения коэффициентов диффузии ионов солей в мембранах с радиусами пор от 5 до 8 нм при pH = 6,5–7,5 в целом соизмеримы для ионов солей. Выявленные особенности диффузии ионов солей в ПА мембранах (экспоненциальная зависимость коэффициента диффузии от радиуса пор мембран, величина pH) и сопоставление полученных данных с имеющимися солей, позволяют определить перспективы и условия их разделения в ПА-мембранах.

**Ключевые слова:** диффузия, мембраны, ионы солей, полиамиды, очистка воды

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