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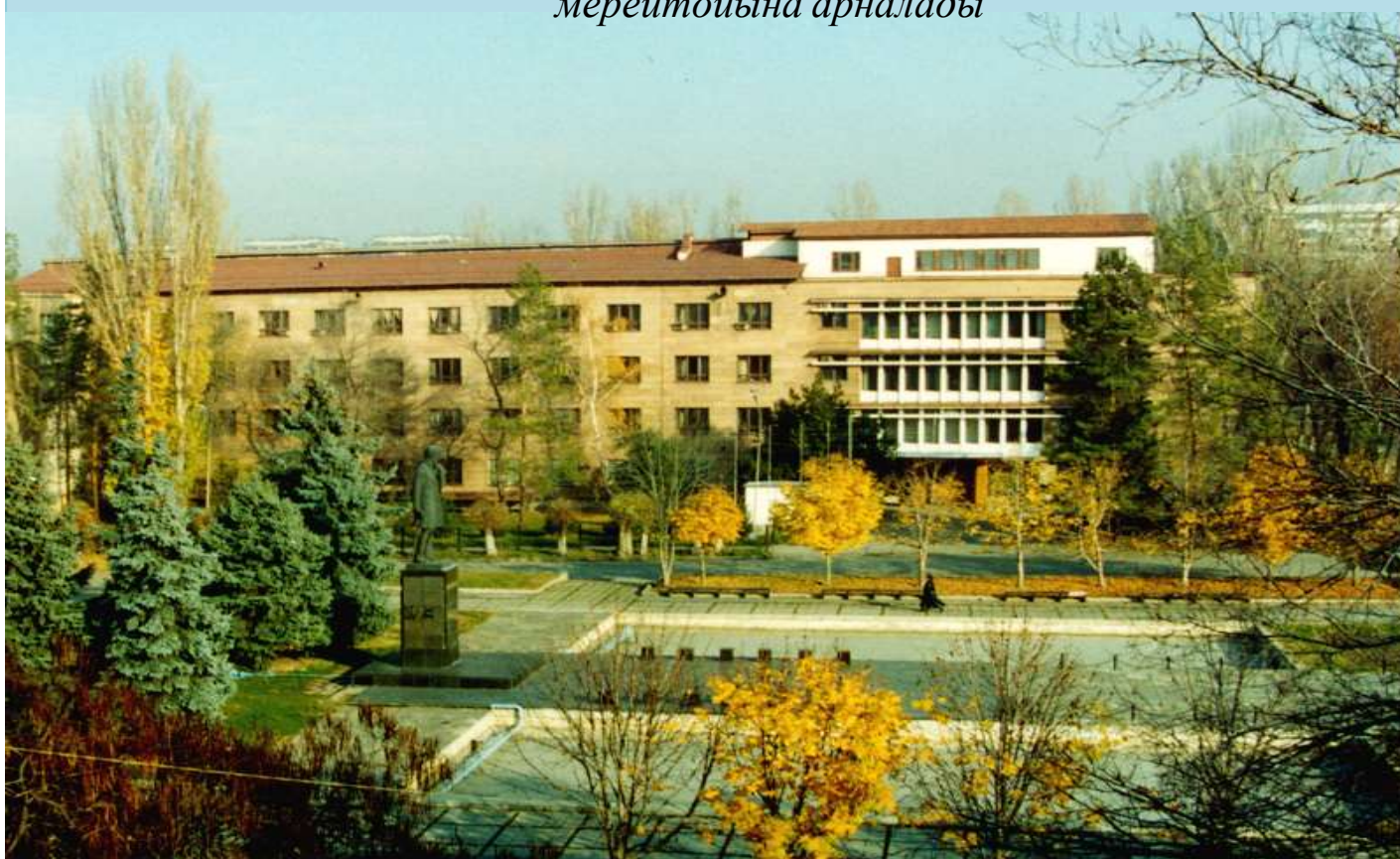
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СОДЕРЖАНИЕ

Секция 1. СОВРЕМЕННЫЕ НАПРАВЛЕНИЯ РАЗВИТИЯ ОРГАНИЧЕСКОЙ, НЕОРГАНИЧЕСКОЙ, ПОЛИМЕРНОЙ ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

KHUTORYANSKIY V. V. Poly(2-oxazolines) as a class of water-soluble polymers promising for pharmaceutical applications	15
KUDAIKULOVA S.K., ZHUBANOV B.A., ABADIE M.M. New composite films based on polyimide: An exemplary scientific collaboration between France and Kazakhstan in the field of high temperature polymers	17
ZEYNALOV E.B. Mass spectrometric analysis of components of diesel fractions	19
КОПИШЕВ Э.Е. Теория эффекта дистанционного взаимодействия гидрогелей	20
TAVATADZE L.B., ARCHVADZE K.T., CHACHAVA I.R., PIRTSKHELIANI N.A., GULBANI D.B. Synthesis and research of the bromine-containing biopolymers	23
ӘБДІҚАРИМОВ М.Н., ТҮРГҮМБАЕВА Р.Х. Жаймалайтын және құрамында карбоксил бар сұйық каучуктер негізіндегі полимерлік композициялар	25
БҮРКЕЕВ М.Ж., БОЛАТБАЙ А.Н., ТОЛЕУОВҰ.Б., ДАВРЕНБЕКОВ С.Ж. Кинетика термического разложения сополимеров полиэтиленгликольфумарта с акриловой кислотой	30
БҮРКЕЕВ М.Ж., ТАЖБАЕВ Е.М., ЖҮНІСОВА М.С., ШИБАЕВА С.Р., КАЖМУРАТОВА А.Т. Синтез полифункциональных полимеров для получения иммобилизационных материалов	32
ДЖАМАНБАЕВА Г.Ж., ТАУСАРОВА Б.Р. Придание полифункциональных свойств целлюлозным текстильным материалам с применением с золь-гель технологии	34
ТҮРГҮМБАЕВА Р.Х., ӘБДІҚАРИМОВ М.Н. Мұнайбитумды жыныстардың иқ-спектрлері	38
BYZOVA YU.S., OSTROVNOY K.A., GORSHKOVA T.A., SAVELYEVA P.O., ZAGIEVA A.V. Recycling of spent polyisobutylene in asphalt concrete materials	49
ДЖУСИПБЕКОВ У.Ж., ТОРЕБЕКОВ О.Т., УТЕЛБАЕВ Б.Т., КОЖАБЕКОВА Н.Н. Получения нафталина из каменноугольной смолы «сары-арка спецкокс»	54
KOVRIGINA T.V., KHAКIMVOLATOVA K.KH., MELNIKOV YE.A., BEGENOVA B.E., CHALOV T.K. Polyelectrolytes with nanosized pores on the basis of nitrogen- and oxygen-bearing compounds and some polyamines	55
KHARLAMOVA T.V., GABDRAKIROV A.V. Functionalization of alizarin using compounds containing saturated cyclic carboxylic acids fragment	59
KHARLAMOVA T.V., GABDRAKIROV A.V., SEIDAKHMETOVA P.B. Effect of monosubstituted purpurin derivatives containing a saturated cyclic fragment on candida albicans	62
PRALIYEV K.D., YU V.K., MALMAKOVA A.E., KALDYBAYEVA A.B., SERGAZY A. New heteroorganic systems based on 1-(3-aminopropyl)imidazole	65
ӘБДІКЕРІМ М.С., АЗИМБАЕВА Г.Е. Xanthium strumarium өсімдігінің сабағы құрамындағы суда еритін дәрумендерді капиллярлы электрофорез әдісімен анықтау	66
BAIMYRZA P.A., KUDAIBERGENOVA B.M., IMINOVA R.S., KAIRALAPOVA G.ZH. Obtaining and studying the properties of organic biocomposite chitosan/pva/bentonite clay film	68
ТАУСАРОВА Б.Р., САДЫКОВА М.Е. Модификация льняных материалов наночастицами диоксида титана	70
МАЛИМБАЕВА З.Б., САПАРБЕКОВА И.С., САФАРМАМАДЗОДА С.М. Торлаушы агенттің әртүрлі мөлшерінде синтезделген псевдоматрицалардың ерекшеліктері	72
ГРАЖУЛЯВИЧЮС Ю.В., ТОТХУСҚЫЗЫ Б. Аномальная сорбция ионов иттрия взаимоактивированными гидрогелями в интерполимерной системе полиметакриловая кислота-поли-4-винилпиридин	76
ТЛЕКБАЙ Г.Т., ИСМАИЛОВ Д.В., ӘУЕЛХАНҚЫЗЫ М., НӘЖІПҚЫЗЫ М. Көміртекті наноматериалдар негізіндегі композиттер алу	84
МЫРЗАХМЕТОВА Н., ЫСҚАҚ Л., ТУРАЧ Е. Молекулалық-таңбаланған полимерлер синтезі	85
ТАУСАРОВА Б.Р., ШАЙХОВА Ж.Е., АБИЛКАСОВА С.О., КАЛИМОЛДИНА Л.М.	

POLYELECTROLYTES WITH NANOSIZED PORES ON THE BASIS OF NITROGEN- AND OXIGEN-BEARING COMPOUNDS AND SOME POLYAMINES

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The analysis of literature data shows that nitrogen-bearing anionites are promising for sorption isolation and concentrating from industrial solutions of transition metals. Ionites of retiform structure differing with high-speed sorption are of great interest[1]. It was shown that ionites on the basis of glycidil ether of resorcin(DGER), vinyl ether of monoethanolamine(VEMEA), allylbromide (AB) and amine extract ions of Cu²⁺ and Ni²⁺ [2].

Methods of membrane technology are increasingly used in various fields of industrial production, and therefore physical-chemical and electrochemical property demands to the ion-exchange membranes are raised. Currently directed search for the source of reactive compounds and synthesis based on these different types of membranes for electrodialysis processes is carried out.

Polyelectrolytes were obtained by polycondensation of diglycidil ether of resorcin, vinyl ether of monoethanolamine, allylbromide and amines (hexamethylenediamine-HMDA, polyethylenimine – PEI, polyethylenepolyamine – PEPA). Temperature is 50-70°C, durability – 7 h.

Composition and structure of ionites have been researched by means of IR-spectroscopy, elemental and chemical analysis.

Distinctive frequencies (cm⁻¹) of epoxy groups (810-950, 1250, 3000-3050) are not available in spectrums of synthesized ionites, that evidences on its chemical conversion. Lines of deformation vibrations N-H (1490) and stretching vibrations C-N (1270) of amine groups compounds, asymmetrical stretching vibrations of ether group C-O-C (1100) are available. Absorption in the area of 1600 cm⁻¹, conditioned by stretching vibrations of benzene ring, and confirms aromatic character of these compounds.

The most effective amining reagent is HMDA (see schedule 1).

Schedule 1. Some characteristics of synthesized ionites

Ionite	Static Exchange Capacity (SEC), mg-equiv/g	Specific volume, ml/g
1 DGER:VEMEA:AB:HMDA	8,5	4,5
2 DGER:VEMEA:AB:PEI	7,0	3,8
3 DGER:VEMEA:AB:PEPA	5,8	3,0

Synthesized ionites have high sorption capacity (mg/g) to transition metal ions (SEC_{Cu} 644,0; SEC_{Ni} 500,6), thus may be used in hydrometallurgy for such metals to be extracted from industrial solution.

In figure 1 isotherms of sorption of ions of platinum metals by the new polyfunctional anionites on the basis of DGER, VEMEA, AB and PEPA and DGER, VEMEA, AB and PEI are offered. As shown in figure, more sharp stroke 1, 3 curved denotes that ions of palladium are absorbed by synthesized anionites from the chloride solutions more better than cations of platinum.

Isotherms of sorption of ions Pd (II) for both anionites are absolutely identical, that is ionites

regardless of their structure are extracting the chlorinecomplexes of palladium in the same degree. Presence of polymer in the structure on the basis of DGER, VEMEA, AB and PEI iminegroups practically does not influence on absorption of Pd (II) ions. Isotherms of sorption of Pt (IV) ions from the H_2PtCl_6 solutions by the anionites, as rising concentration of ions of platinum to 0,5g/l the importance of exchange capacity is sharply increasing, and at more higher content is insignificantly changing. Maximal sorptive capacity on ions of platinum (IV) at their extraction from the solutions in which its concentration is equal to 1,464 g/l, and making for anionites on the basis of PEPA and PEI 234,4 and 263,6 mg/g is observed accordingly. Anionite on the basis of PEI, as shown in figure 1, is possessing more selectivity with respect to ions of platinum (IV) than ionite on the basis of PEPA.

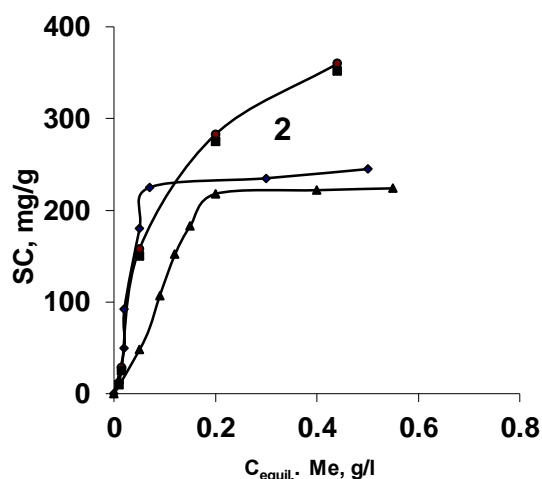


Figure 1. Isotherms of sorption of Pd (II) (1,3) and Pt (IV) (2,4) ions by anionites on the basis of PEPA (1,4) and PEI (2,3)

We also used DGER, VEMEA, AB as feedstock for obtaining ion-exchange membranes, and polyvinylchloride (PVC) as thermoplastic polymer. Impact of ratio of starting components and its nature for electrochemical and physical-mechanical indices of forming membranes has been tested with the aim to receive optimal process conditions. Determining of their main electrochemical characteristics was made on lab electro dialysis cells. It was discovered that the largest SEC (4,2 mg-equiv/g) have ion-exchange membranes when mass correlation of DGER+VEMEA+AB+amine :PVC=70: 30 mass.% [3]. At that samples have low specific electric resistivity and rather high mechanical strength for plain membranes. Further increase of amine concentration slightly influences on change of SEC membranes (see schedule 2) [4].

Schedule 2. Electrochemical properties of interpolymeric membranes on the basis of VEMEA, DGER, AB and connecting PVC which are received in the presence of different polyamines

Membranes on the basis of VEMEA:DGER:AB in the presence of	SEC on 0,1 n to solution HCl, mg-equiv/g	Electrical resistance, Om-sm	Transport number, %	Specific water permeability, $K \cdot 10^{-14}$, $sm^3 \cdot sec/g$
PEPA	2,9	90	0,98	1,3
HMDA	3,2	65	0,97	1,8
PEI	4,2	54	0,98	1,9
MA-40	3,4	240	0,94	—

Structure of obtained ion-exchange membranes containing different functional groups has been studied by methods of sample and mercurial porometric (figures 2, 3).

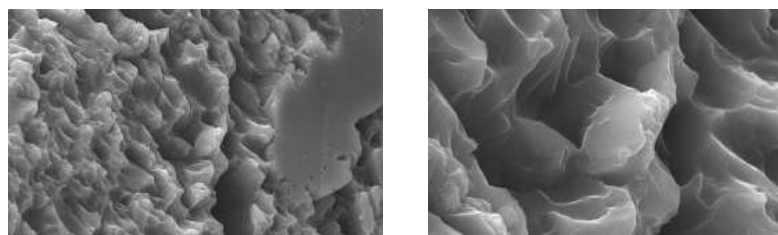


Figure 2. Microphotographies of samples of synthesized ion exchange membranes

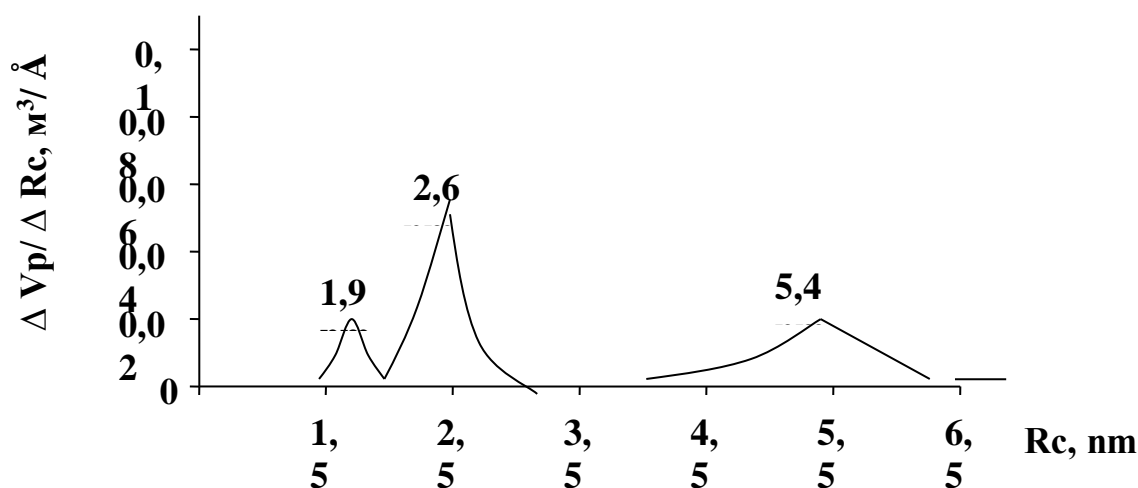


Figure 3. Location of pores with radius in the synthesized ion exchange membranes on the basis of VEMEA, DGER, AB and PEPA

Study of relative and volumetric membrane porosity represents definite theoretic and practical interest, as its number and reciprocal position in ionite influences to sorption and electrochemical characteristics of final products. Structure of dry samples is gradually differ from the structure in working turgid state, as far as swelling result in frequent increase of interstice volume due to aqation of functional groups.

Porosity of ion-exchange membranes of interpolymetric type based on DGER, VEMEA, AB and PEPA depends on durability of cure and character of source monomers. It was discovered that they are characterized by specific porosity from 0,2 to 2,0 mg/g, which is decreased when increasing durability of cure.

It is showed, that samples synthesized at 60⁰C, have the most homogeneous porosity structure in all layer thickness. Rise in temperature to 80⁰C and increase of duration of thermocuring to 24 hours result in SEC growth and decreasing of relative membrane porosity from 12,9 to 0,8 cm³/g depending on the character of starting monomers. Thus, the rise in temperature results in reduction of interstice size and accordingly decreasing of water resistance [5].

Study of porosity structure of synthesized interpolymer membranes by means of mercuric intersticemetric showed, that samples mainly consists of interstices of 1,9-2,6 nm in radius and lesser number of interstices of 5,4 nm in radius [6]. Relative specific membrane porosity composes 6,8-1,0 cm³/g [7,8].

Thus, ion-exchange polymers and membranes with high sorption, physical-mechanical and electrochemical characteristics are synthesized on the basis of available capable to reaction monomers and olygomers. The size of interstices of obtained membranes has been determined by methods of sample and mercuric intersticemetry. Sizes and maximal narrow interstice allocation by

radius of synthesized membranes point to their identity by structure with homogeneous ones that opens immense perspectives for their practical use.

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