

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

5 (443)

SEPTEMBER – OCTOBER 2020

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген № KZ66VPY00025419 мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Тақырыптық бағыты: *химия және жаңа материалдар технологиясы саласындағы басым ғылыми зерттеулерді жариялау.*

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28; 219, 220 бөл.; тел.: 272-13-19; 272-13-18,
<http://chemistry-technology.kz/index.php/en/arhiv>

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Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д. В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекенжайы: «NurNaz GRACE», Алматы қ., Рысқұлов көш., 103.

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«Известия НАН РК. Серия химии и технологий».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан № **KZ66VPY00025419**, выданное 29.07.2020 г.

Тематическая направленность: *публикация приоритетных научных исследований в области химии и технологий новых материалов.*

Периодичность: 6 раз в год.

Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,

<http://chemistry-technology.kz/index.php/en/arhiv>

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Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142, АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», каб. 310, тел. 291-62-80, факс 291-57-22, e-mail: orgcat@nursat.kz

Адрес типографии: «NurNaz GRACE», г. Алматы, ул. Рыскулова, 103.

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News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan No. **KZ66VPY00025419**, issued 29.07.2020.

Thematic scope: *publication of priority research in the field of chemistry and technology of new materials*

Periodicity: 6 times a year.

Circulation: 300 copies.

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,

<http://chemistry-technology.kz/index.php/en/arhiv>

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Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: «NurNaz GRACE», 103, Ryskulov str, Almaty.

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2020.2518-1491.87>

Volume 5, Number 443 (2020), 108 – 115

UDC 661.182.547.721

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SYNTHESES OF CATION EXCHANGER WITH MACROPOROSITY AND INVESTIGATING SPECIFIC PROPERTIES

Abstract. Obtained new strongly acid cation exchanger of macroporous structure based on furfural and dipheniloxide. The optimal amount of the poreformed agent and the molar ratio of the reacting substances were determined. Initially results showed that the polymer matrix using camphor as pore forming agent present a uniform surface with inter-connected pores and adding camphor into the polymer matrix could attain more abundant pores than adding n-heptane. We studied the components, surface and pore structures of the cation exchanger by Fourier transform infrared spectroscopy and scanning electron microscopy (SEM). SEM observations showed that the resin abounded in macropores as large as 7.4 to 22.6 μm both in the surface and the interior. The parameters of the porous structure of the samples are calculated using by equation BET (Brauner., at al.) and the total pore volume of ion exchangers and the radius of submicroscopic capillaries were determined. Finally dates testing prototypes under application conditions, allow us to recommend this cation exchanger for sorption of small radius ions at high speed, as fundamentals upon receipt of ion exchangers, etc.

Keywords: cation exchanger, furfural, pore-forming agent, exchange capacity, bulk density, specific volume, porosity, selectivity.

Introduction. The areas of use of ion exchangers are expanding annually, which determines the range of research and technological work on the synthesis of ion exchangers following sorption properties. [1-5]. The issue of improving the kinetic and mechanical properties of ion-exchange polymers that has recently become particularly acute has found a rather successful solution due to the creation of macroporous structures. In the literature, there are a large number of reports on the methods of obtaining copolymers of macroporous structure by copolymerizing vinyl derivatives in the presence of various additives, and the number of works on the preparation of macroporous ion exchangers on polycondensation matrices is very limited [6-7].

It is known that in a conventional copolymer, the gaps in the molecular network formed during the crosslinking process are micropores. When swelling in aromatic and chlorinated hydrocarbons, the solvent penetrates into them, greatly expanding the molecular network. The mechanism of swelling of the macroporous copolymer is different. Its porosity is similar to that of a sponge. The blowing agent fills the free space in the copolymer, which is accompanied by only a slight expansion of the molecular network.

Scientist of work (8-9) reported dyes were immobilized under mild conditions by a sol-gel process which generates a high porosity for easy analyte access.

Methods. Three-necked flask equipped with a reflux condenser and a mechanical stirrer with a bolt and a thermometer. Diphenyloxide putted into flask and 45% solution of sulfuric acid added. The mechanical stirrer speed of 120 round a minute into the flask during the reaktion. After a few time at 30-40°C furfural added drop by drops. Pore-forming agents (n-heptane, camphor) added to the reaction environment from 20 to 60% by the total weight of monomers. The temperature was raised to 70-80°C and

at this temperature, during 90–100 minutes gel was formed. Product transferred to a porcelain dish and dried in the air at ambient temperature. The dried polymer was milled to a grain diameter $d_g = 0.25\text{--}0.5$ mm. Following the granules of obtaining polymer spread to the lawn covered by blanket for distilling over from pore-formed substances using steam. The duration of process 3 hours. Later dry process carried out in two stages; initially at 80–90°C, then at 100°C until it reached the air – dry state.

The finished polymer exposed to the sulfonation. The polymer swelled in concentrated sulfuric acid was placed in a three-neck flask with a mechanical stirrer and reflux condenser. The sulfonation conducted with 92–95% sulfuric acid, the molar ratio of polymer and acid was 1:6. The sulfonation temperature 70°C for 6 hours. To avoid deformation of the polymer matrix after sulfonation, the cooled polymer was washed with sulfuric acid, decreasing the concentration successively to 75, 50, 25 and 10% and then washed with distilled water until neutral wash water, then the resulting cation exchanger was dried at 80–90°C in a drying cabinet [10–13].

The microstructure and morphological studies of the surface were carried out using a scanning electron microscope 10(Carl Zeiss) and the compositions of the ion exchangers were determined using an energy-dispersive elemental analyzer brand EDS (Oxford Instrument)– Aztec Energy Advanced X-act SDD. Investigation of the dimension of microporous cation exchanger was performed using SEM device (Quanta 3D 200i) [14–15]

Strong acid cation exchangers adsorption isotherms were measured on a high-vacuum installation with mercury valves and Mac-Ben quartz weights in the range of 0–100% relative humidity at $25 \pm 0,3^\circ\text{C}$. Calculated absolute adsorption isotherms of porous bodies to determine the specific surface and pore distribution over the radius at low temperature using by BET equation [16–17].

Results and discussion. By polycondensation of diphenyloxide and furfural in the presence of pore-forming agents, n-heptane and camphor, copolymers of macroporous structure were obtained [18–19]. Properties of obtained ion exchanger depends on degree of crosslink agent and the amount of pore-forming agents. Studied the molar ratio of furfural range from 1 to 2 moles per mole of dypheniloxide and the amount of pore-forming agent varies from 20 to 60% of the total weight of monomers.

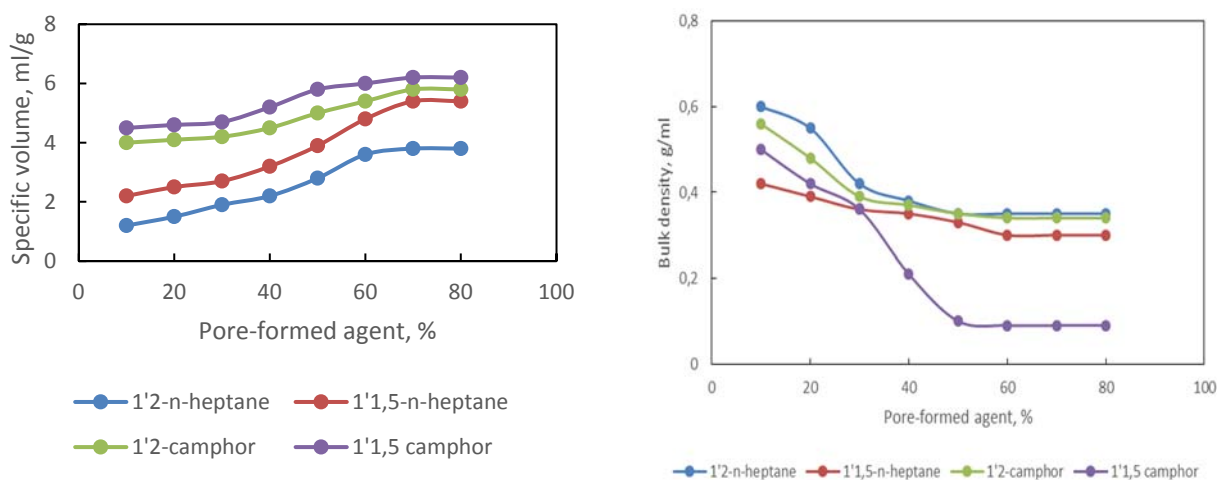


Figure 1. Dependence of bulk density and specific volume on the content of the pore-formed agent at various molar ratios of dypheniloxide and furfural

Figure 1 shows that with an increase in the amount of pore-formed agent present during polycondensation, the bulk density of polymers decreases and the specific volume increases. In our opinion, the case of this situation is the transition from the gel to the macroporous structure depends on the content of the cross-agent in the copolymer and on the amount of the pore-formed agent entered into the reaction environment. The optimal molar ratio of the polycondensation reaction between dypheniloxide and furfural are 1'1,5 and amount of pore-formed agent is 60%.

The study of changes in the specific volume and amount of solvent absorbed by the copolymer during swelling suggests that the swelling mechanism changes from a conventional structure to a macroporous one: the solvent fills the free space in the copolymer, which is accompanied by a relatively small

expansion of the molecular network. It had founded that macroporous copolymers swelled not only in conventional “swelling” agents, but also in solvents in which conventional copolymers do not swell. Figure 2 demonstrate the dependences of the amount of toluene and cyclohexane absorbed during swelling by the ion exchanger on the inserted pore-forming agent.

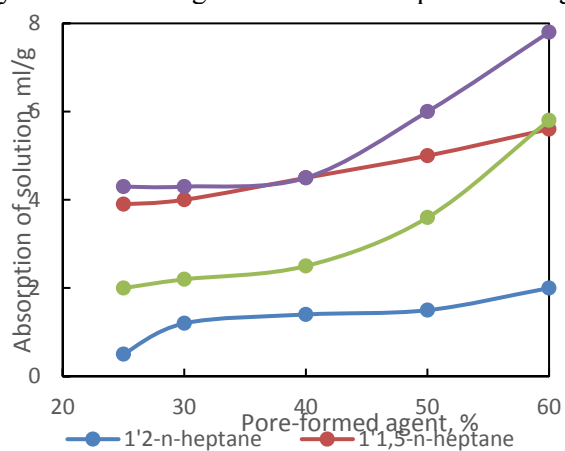


Figure 2 - Dependence of absorption of solution on the content of the pore-formed agent at various molar ratios of dyheniloxide and furfural

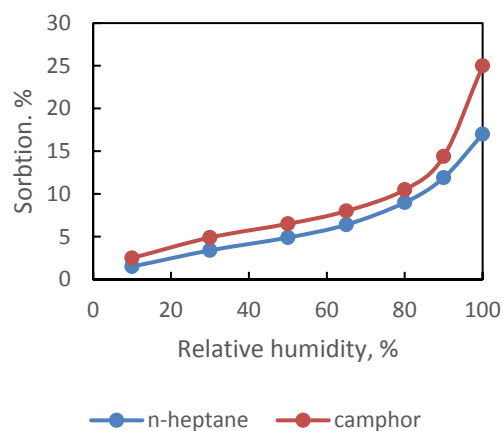


Figure 3 - The influence of the nature of the pore-formed agent on the sorption of water vapor by cation exchanger at 25 °C

The direction of the curves figure 2 shows that as the amount of the blowing agent increases, the amount of absorbed toluene and cyclohexane increases; at the same time, the degree of swelling decreases in toluene and increases in cyclohexane. This again shows that the structure of the cation exchanger influenced simultaneously by the degree of crosslinking and the amount of introduced pore-forming agent.

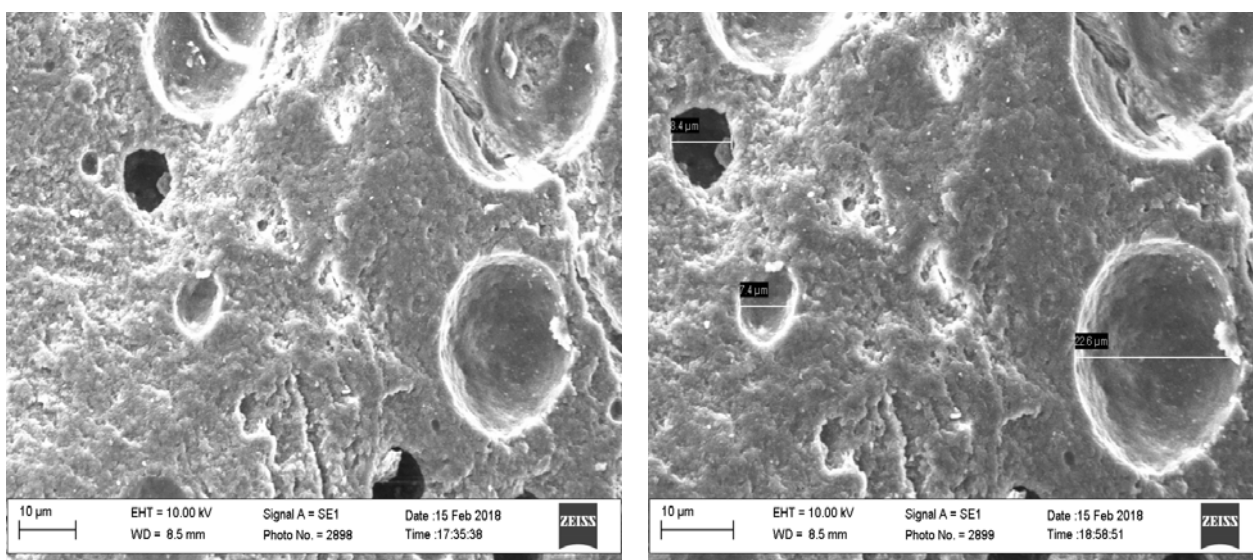


Figure 4 - Electronic images pores of obtaining cation exchanger

Further studied the influence of the nature of the pore-forming agent on the sorption of water vapor by cation exchanger in figure 3. The results of water vapor sorption by ion exchanger predicated once again that camphor as pore-formed agent suitable for polymer matrix and given the better dates than n-heptane.

Using by scanning electronic microscopy equipment investigated high accuracy poros sizes of obtaining cation exchanger, which containing poros from 7.4 to 22.6 μm. Once again, the results confirmed that for macroporous cation exchanger reasonable pore-formed agent is camphor.

Determining of specific surface area and pore distribution over the radius at low temperature is an important indicator for comparison obtaining macroporous cation exchanger with existing cation exchangers. Depending on the porosity and pore size distribution of the particle, the specific surface area

is influenced by size, shape, and roughness. When the particle structure presents nil or low porosity, the specific surface area of the particle is a function of these other attributes. Under these circumstances the specific surface area typically presents a stronger correlation with dissolution rate of the particle if the dissolution rate is controlled by external mass transfer.

The specific surface area is typically characterized by the physical adsorption of a gas (argon, krypton, or nitrogen) on the surface of the sample at cryogenic temperature. Gas adsorption can be determined by volumetric, gravimetric, or flux methods. The volume of gas adsorbed on a monolayer over the surface of the particles is determined according to the BET equation (Brunauer et al.), and the specific surface area is calculated based on molar volume of the gas and the average area occupied by the gas molecule [18].

For this aim calculated absolute adsorption isotherms of porous bodies using by BET equation. The capacity of the monolayer determined by the equation:

$$\frac{P_i}{x(P_1^0 - P_i)} = \frac{1}{x_m \cdot C} + \frac{C-1}{x_m \cdot C} \cdot \frac{P}{P_0}$$

where: P – is the equilibrium vapor pressure of the sorbate over the sorbent; P_0 – is the saturated vapor pressure of sorbate at the same temperature; X – is the amount of the sorbed substance, g/g; X_m is the amount of a substance in a continuous monomolecular layer, g/g; C – is a constant representing the ratio of the lifetime of the molecules in the first layer and the liquid, respectively.

According to the equation, the dependence of $\frac{P}{(P_0 - P)} \cdot \frac{P}{P_0}$ on $\frac{P}{P_0}$ should have the form of a straight line

with the slope $S = \frac{C-1}{x_m \cdot C}$ and cut off the ordinate segment $i = \frac{1}{x_m \cdot C}$ Solving the system of equations

gives the value of the monolayer capacity: $x_m = \frac{1}{S+i}$ and energy constants $C = \frac{S}{i} + 1$

Based on results of applying equation BET obtained following dates, which presented in table 1.

The ion exchange resins are macroporous, have a surface area of at least 50 m²/g, and an average particle size of at least 20 micrometers [19]. As you see that obtaining macroporous cation exchanger contained high specific surface area about 150 m²/g and up to 20 micrometers respectively.

Table 1 - Effect of the nature of the pore-forming agent on the capillary-porous structure of the samples

Sample	Pore-forming agent	
	n-heptane	camphor
Monolayer capacity, X_m , g/g	0.0325	0.0420
Specific surface area, S_{sp} , m ² /g	114.24	147.63
Total pore volume, W_0 , sm ³ /g	0.17	0.25
Radius of submicroscopic capillaries, r_c , Å	29.76	33.87

Researches related to investigation of structure synthesis polymers (PI) involved by scientists [20]. Crosslinked sulfonated polymer (PI) types have been developed for use as cation exchange membranes. The sulfonated PIs have excellent proton conductivity and a low cost of preparation. Therefore in the process of regeneration of ion exchange resin, it is necessary to achieve the most complete desorption of both noble metals and impurities. [21]. However, there are significant differences between ion-exchange membranes and ion-exchange resins concerning the polymer structures which are primarily due to the differences in size and shape between ion-exchange beads and ion-exchange membrane sheets. In both cases the fixed ion-exchange groups lead to a swelling of the polymer when it is in contact with an aqueous solution. The degree of swelling depends on the ionic strength of the solution and on the degree of cross-linking of the polymer [22].

The main properties and requirement for cation exchangers are cation exchange capacity. In our case, entered pore-formed agents in the several quantities into polymer matrix following this exchange capacity differed each other depending on form of cation exchanger. In table, 2 presented dates of sorption properties of obtained macroporous cation exchangers depending on the nature of the pore-forming agent and its quantity.

Table 2 - Exchange capacity of macroporous cation exchangers depending on ion form

Pore-formed agent	Amount of Pore-formed agent, %	Exchange capacity, meq/l							
		NaCl 0.1N	NaOH 0.1N	0.1N CaCl ₂		0.1N MgSO ₄		0.1N CuSO ₄	
				Ion form					
				H-	Na-	H-	Na-	H-	Na-
n-heptane	30	0.72	3.2	0.55	1.75	0.65	1.75	0.4	1.1
	60	0.84	3.8	0.8	1.2	0.8	1.85	0.6	1.4
camphor	30	0.95	3.8	0.95	2.0	1.0	2.0	1.2	1.2
	60	1.32	4.8	1.45	2.35	1.45	2.35	1.4	1.5

Its value depends on the number of acid groups of the ion exchanger, the degree of their dissociation, as well as the nature and concentration of the exchanging ions. The exchange capacity of sodium form higher than hydronium forms. This process explained with radius of exchanging ions, as they activity properties.

Conclusion. Thus, as a result of the research, obtained strong acid cation exchangers and investigated the dependence of their properties on the degree of macroporosity. The presence of macropores explains the ability of the copolymer to absorb also aliphatic and cyclic compounds in which the usual copolymer does not swell. This also explains the increased mechanical strength of ion exchangers based on macroporous copolymers under operating conditions, since during sorption and desorption their volume remains almost constant. At the same time, macroporosity creates a large exchange surface, contributes to the rapid diffusion of ions and the sorption.

Based on the data obtained, it is possible to conclude that when polycondensation is present in the presence of the selected type of pore formers, cation exchangers are obtained with a macroporous structure that approaches the structure of rigid sorbents, and the degree of macroporosity increases in the investigated interval with increasing cross-agent content and the amount of pore-forming agent.

Acknowledgments. This work was carried out within the framework of the project of the Republic of Uzbekistan PZ-20170927346 Development of technology of ion-exchange polymers of polycondensation type for wastewater treatment.

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МАКРОСАҢЫЛАУЛАРМЕН КАТИОНАЛМАСТЫРҒЫШТАҒЫ СИНТЕЗ ЖӘНЕ ЕРЕКШЕ ҚАСИЕТТЕРДІ ЗЕРТТЕУ

Аннотация. Иониттегі макросаңылаулар оған қалыпты жағдайда сополимерлерде болмайтын алифатикалық және циклді қосылыстарды сіңіруге мүмкіндік береді. Сонымен қатар, жұмыс барысында макросаңылаулы сополимерлерге негізделген иониттердің механикалық беріктігінің арту жағдайын түсіндіреді, сорбция және десорбция барысында олардың көлемі өзгермейді. Онда үлкен макросаңылаулық алмасу бетін қалыптастырады, иондардың жылдам диффузиясына және ірі молекулалар сорбциясына әсер етеді.

Белгілі болғандай, қарапайым сополимерде тігілу үдерісі барысында түзілетін молекулалық торда аралық микросаңылау ретінде қарастырылады. Ароматты және хлорланған көмірсутекте ісіну кезінде еріткіш оларға өтіп, молекулалық торды нақты шамада кеңейтеді. Макросаңылаулы сополимердің ісіну механизмі әртүрлі. Оның саңылаулығы серпімділік кеуектігіне ұқсас. Саңылау түзуші сополимердегі бос кеңістікті толтырады, ол молекулалық тордың шағын кеңеюі арқылы жүзеге асады. Макросаңылау қарапайым сополимер ісінбейтін сополимердің алифатты және циклді қосылыстарды сіңіру қабілетін түсіндіреді.

Жоғарыда келтірілгенді ескеріп, түрлі саңылау түзуші заттардың (н-гептан және камфара) қатысуымен дифенил оксиді мен фурфурол поликонденсациясы арқылы макросаңылаулы құрылымның сополимерлері

алынады. Саңылау түзуші заттың оңтайлы мөлшері және реакцияға түсетін заттардың молярлық қатынасы анықталады. Бастапқыда нәтижелер көрсеткендей, камфора қолдану негізінде полимерлі матрица саңылау түзуші агент ретінде байланыстырылған саңылауы бар біртекті жоғарғы бет түрінде алынады, ал полимер матрицасына камфорды қосу н-гептанды қосуға қарағанда көп мөлшерде саңылау түзеді.

Макросаңылаулы ион алмастырғыш кеуектің негізгі сипаттамалары, оның ішінде саңылаудың жалпы көлемі ($\text{см}^3/\text{г}$), саңылаудың орташа тиімді радиусы, олардың радиусы бойынша саңылаудың таралуы, меншікті жоғарғы беті ($\text{м}^2/\text{г}$) $25 \pm 0,3$ °C температурада 0-100% салыстырмалы ылғалдылық аралығында сынап қақпағы мен Мак-Бен кварц таразымен жоғары вакуумды қондырғыда зерттеледі. Фурье түрлендіргіш ИК-спектроскопиясы мен сканерлеуші электронды микроскоп (СЭМ) арқылы катионит құраушылары, жоғарғы беті және саңылаулы құрылымы зерттеледі. СЭМ арқылы бақылау жұмыстары көрсеткендей, шайыр құрамының жоғарғы бетінде, ішінде 7,4 тен 22,6-ға мкм дейінгі өлшемде макросаңылаудың мөлшері көп байқалады.

Үлгілердің саңылаулы құрылымының параметрлері БЭТ (Браунэр-Эммит-Теллер) теңдеуі бойынша есептеледі және ионалмастырғыш саңылаудың жалпы көлемі мен субмикроскопиялық капиллярлар радиусы анықталады. БЭТ теңдеуінің координаталарындағы су буының адсорбциялық изотермалары төмен қысымды аймақта түзу сызықты сипатқа ие. Бұл алынған СКДФ-МП макросаңылаулы катиониттің су буының сорбциялық изотермаларын сипаттайтын БЭТ теңдеуінің қолданылу тиімділігін айқындайды. Өнеркәсіпте жасалатын макросаңылаулы иониттерде саңылау көлемінің қосындысы 0,2-1,0 $\text{см}^3/\text{г}$, меншікті жоғарғы беті 30-дан 200 $\text{м}^2/\text{г}$ дейін, саңылаулардың үлкен радиусы 5-60 нм құрайды. Өндірістік иониттермен салыстырғанда, біз алған мәліметтер оның көрсеткіштерінен төмен емес. Нәтижесінде пайдалану жағдайындағы тәжірибелік үлгілерді сынау күндері бұл катионитті ионалмастырғыштар алуға негіз ретінде жоғары жылдамдықта аз радиусты иондарды сорбциялауға ұсынуға мүмкіндік береді.

Сорбциялық изотермалар негізінде таңдалған типтегі саңылау түзушілердің қатысуы арқылы полимер алуға байқалатын саңылау сипаттамалары есептеледі, макросаңылаулы құрылымды катионит түзіледі, ол қатты сорбенттер құрылымына ұқсас, ал зерттелетін аралықта саңылауды түзу мөлшерін арттырумен макросаңылау дәрежесі жоғарылайды.

Түйін сөздер: фурфурол, катионит, саңылау түзуші зат, алмасу сыйымдылығы, көлем тығыздығы, меншікті көлем, кеуектік, селективтік.

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СИНТЕЗ КАТИОННООБМЕННИКА С МАКРОПОРИСТОСТЬЮ И ИССЛЕДОВАНИЕ ОСОБЫХ СВОЙСТВ

Аннотация. Наличие макропор в ионите позволяет ему поглощать алифатические и циклические соединения, что недоступно обычным сополимерам. Этим же объясняется повышенная механическая прочность ионитов на основе макропористых сополимеров в условиях эксплуатации, так как при сорбции и десорбции их объем остается почти постоянным. Вместе с тем макропористость создает большую поверхность обмена, способствует быстрой диффузии ионов и сорбции молекул большого размера.

Известно, что в обычном сополимере промежутки в молекулярной сетке, образующиеся в процессе сшивания, являются микропорами. При набухании в ароматических и хлорированных углеводородах растворитель проникает в них, значительно расширяя молекулярную сетку. Механизм набухания макропористого сополимера иной. Его пористость подобна пористости губки. Порообразователь заполняет свободное пространство в сополимере, что сопровождается лишь незначительным расширением молекулярной сетки. Наличие макропор объясняет способность сополимера поглощать также алифатические и циклические соединения, в которых обычный сополимер не набухает. Этим же объясняется повышенная механическая прочность ионитов на основе макропористых сополимеров в условиях эксплуатации, так как при сорбции и десорбции их объем остается почти постоянным.

Учитывая вышесказанное, поликонденсацией дифенилоксида и фурфурола в присутствии различных порообразователей (н-гептана и камфары), были получены сополимеры макропористой структуры. Определяли оптимальное количество порообразователя и молярное соотношение реагирующих веществ. Первоначально результаты показали, что полимерная матрица с использованием камфары в качестве порообразующего агента представляет собой однородную поверхность со связанными порами, и добавление камфары в полимерную матрицу может дать более обильные поры, чем при добавлении н-гептана.

Основные характеристики пористости макропористого ионообменника такие, как суммарный объем пор (в см³/г), средний эффективный радиус пор, распределение пор по их радиусам, удельная поверхность (в м²/г) изучена на высоковакуумной установке с ртутным затвором и кварцевыми весами Мак-Бена в интервале относительных влажностей 0-100% при 25±0,3°С. Мы изучили компоненты, поверхностную и поровую структуры катионита с помощью ИК-спектроскопии с Фурье-преобразованием и сканирующей электронной микроскопии (СЭМ). Наблюдения с помощью СЭМ показали, что смола содержала большое количество макропор размером от 7,4 до 22,6 мкм как на поверхности, так и внутри.

Параметры пористой структуры образцов рассчитывали по уравнению БЭТ (Браунэр-Эммит-Теллер) и определяли общий объем пор ионообменников и радиус субмикроскопических капилляров. Изотермы адсорбции паров воды в координатах уравнения БЭТ имеет прямолинейный характер в области низких давлений. Это подтверждает применимость уравнения БЭТ для характеристики изотерм сорбции водяного пара полученного макропористого катионита СКДФ-МП. В производимых промышленностью макропористых ионитов суммарный объем пор составляет 0,2-1,0 см³/г, удельная поверхность от 30 до 200 м²/г, преимущественный радиус пор составляет 5-60нм. Полученными нами данные по сравнению производственных ионитов не уступает своими показателями. Наконец, даты испытаний опытных образцов в условиях применения позволяют нам рекомендовать этот катионит для сорбции ионов малого радиуса на высокой скорости, в качестве основы при получении ионообменников и т. д.

На основании изотерм сорбции были рассчитаны поровые характеристики, показывающие при получении полимера в присутствии порообразователей выбранного типа, образуются катиониты, обладающие макропористой структурой, которая приближается к структуре жестких сорбентов, причем в исследованном интервале с увеличением количества порообразователя степень макропористости увеличивается.

Ключевые слова: фурфурол, катионит, порообразующий агент, обменная емкость, насыпная плотность, удельный объем, пористость, селективность.

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ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Д. С. Аленов, А. Ахметова*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 08.10. 2020.
Формат 60x881/8. Бумага офсетная. Печать – ризограф.
9,6 п.л. Тираж 300. Заказ 5.