Obtaining Ion-Exchange Materials and Studying their Properties

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Abstract

It has been realized modification of phenol-formaldehyde oligomers by acetamide and oksamide. It has been studied ways of obtaining sulphocationites on the basis of phenol-formaldehyde oligomers modified by asetamide and oksamide. To the comparative effect the changing of unmodified phenol-formaldehyde oligomer has been researched. At the end of modification reaction into each benzyl ring there was fed sulfonate group. Main indices of modified oligomers and sulphocationites have been researched. It has been revealed that as a result of including additional functional groups into modified oligomers basic characteristics of sulphocationites have been improved.

Keywords: phenol-formaldehyde oligomers, modified, sulphonation, ionite, acetamide, oksamide.

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İondəyişdirici materialların alınması və xassələrinin tədqiqi

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Xülasə

Fenol-formaldehid oliqomerlərinin asetamid və oksamid ilə modifikasiyası həyata keçirilmişdir. Asetamid və oksamidlə modifikasiya olunmuş fenol-formaldehid oliqomerləri əsasında sulfokationitin alınması üsulları öyrənilmişdir. Müqayisə üçün modifikasiya olmamış fenol-formaldehid oliqomeri də tədqiq edilmişdir. Modifikasiya reaksiyasının sonunda hər bir benzol halqasına sulfoqrup daxil edilmişdir. Modifikasiya olunmuş oliqomerlərin və sulfokationitlərin əsas göstəriciləri tədqiq olunmuşdur. Müəyyən edilmişdir ki, əlavə funksional qrupların modifikasiya olunmuş oliqomerlərə daxil edilməsi nəticəsində sulfokationitlərin əsas xüsusiyyətləri yaxşılaşdırılmışdır.

Açar sözlər: fenol-formaldehid oliqomeri, modifikasiya, sulfolaşma, ionit, asetamid, oksamid.

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Получение ионообменных материалов и изучение их свойств

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Аннотация

Осуществлена модификация фенолоформальдегидных олигомеров ацетамидом и оксамидом. Изучены способы получения сульфокатионита на основе фенолоформальдегидных олигомеров, модифицированных асетамидом и оксамидом. Для сравнительного эффекта было исследовано изменение немодифицированного фенолоформальдегидного олигомера. В конце реакции модификации в каждое бензольное кольцо вводили сульфонатную группу. Исследованы основные показатели модифицированных олигомеров и сульфокатионитов. Выявлено, что в результате включения дополнительных функциональных групп в модифицированные олигомеры улучшились основные характеристики сульфокатионитов.

Ключевые слова: фенолоформальдегидные олигомеры, модификация, сульфирование, ионит, ацетамид, оксамид.

Introduction

Ion-abundant oligomers are used for softening and deionization of water in heat-and-power engineering as well as in other branches for separation and extracting nonferrous and rare metals in hydrometallurgy for purification of recurrent and waste water, in regeneration of electrolytic metallurgy and metal-working wastes, in chemical industry for separation and purification of various substances; they are also used as organic synthesis catalysts [1-3].

Ion-abundant oligomers are of great practical significance for various branches of national economy.

In this respect obtaining sulfonication on the basis of modified phenol-formaldehyde oligomers (PHFO) has been rather actual.

For the synthesis of sulfonication we have obtained modified PHFO through well-known way having used acetamide and oksamide as a modifying agent.

Experimental methods

PHFO modification has been realized in alkaline medium in the laboratory reactor provided with backflow condenser, thermometer and mechanical stirrer. 1,15 mole of phenol, 1.45 mole of formaldehyde (in 37% solution) and 0,02 mole of 25% NH_4OH are placed in the reactor.

The mixture of the components being continuously stirred is heated up to 50-55ºC within 30 minutes and in this very temperature 0,25 mole of modifying agent is partially added into this mixture.

Then the temperature of of the reaction mixture is heated up to 90-95ºC and continuous stirring is going on for 90 minutes more.

Meanwhile the reaction mixture grows turbid and is divided into two layers: the upper layer is watery and the lower one is oligomeric. Oligomer is separated from water, washed in water to neutral reaction and dried in vacuum drying cabinet up to permanent mass.

The output of modified oligomers makes up 70-76%.

The obtained modified oligomers are well solved in acetone, spirit, dioxane and tetrogurofuran.

In order to obtain comparative data in identical terms unmodified PHFO has been synthesized and researched.

To study physical-mechanical characteristics the obtained oligomers (modified by acetamide and oksamide as well as unmodified) were solidified in gradual temperature being heated up to 140ºC within 3 hours [4,5].

The solidification degree of the composition in accordance with its unsolvable part, determined through its extraction in the Soxlete apparatus has made up accordingly 97,8%, 98,5% and 92%.

It has been revealed that, physical-chemical and physical-mechanical characteristics of modified oligomers signify-cantly vary from identical features of unmodified PHFO (table 1).

Results and discussion

It has been studied the swelling kinetics of modified and unmodified PHFO. Swelling is one of the available laboratory control methods of oligomer degree of structuring.

Table 1 – Physical-chemical and physical-mechanical indices of unmodified and modified PHFO

№	Index denomination	Indices		
		Unmodified PHFO	modified PHFO	
			Acetamide	Oksamide
1.	Azotes content, % (weight)	–	2,72	4,96
2.	Content of free phenol, % (weight)	9,7	3,22	2,48
3.	Amount of methylol groups, % (weight)	11,2	8,94	9,76
4.	Amount of hydroxyl groups, % (weight)	17,5	12,42	10,54
5.	Adhesion strength, MPa	1,97	4,56	2,82
6.	Solidity according to Brinel, MPa	220	260	233
7.	Heat-resistance according to Vic, ^{0}C	105	160	157

The higher the degree of structurization, the less is the probability of lower molecular solvent to penetrate into less molecular space of the polymer and the less is the swelling degree. The degree of swelling is changing throughout time. To estimate the ability of oligomers to swell, maximum degree value of swelling should be used. The extent degree of swelling corresponding to the horizontal area of the swelling degree graphic chart is the maximum swelling degree [6-7].

The graphic chart of the swelling degree of modified and unmodified PHFO in spirit-benzyl solution has been constructed.

Figure shows that the swelling degree of modified PHFO is lower than the swelling degree of unmodified PHFO. It is explained with the functionality growth of modified PHFO (fig.).

At the second stage it has been carried out sulfonation of functionalized oligomers.

The sulfonation process was held in the laboratory reactor, of 250 ml capacity, provided with stirrer and backflow condenser.

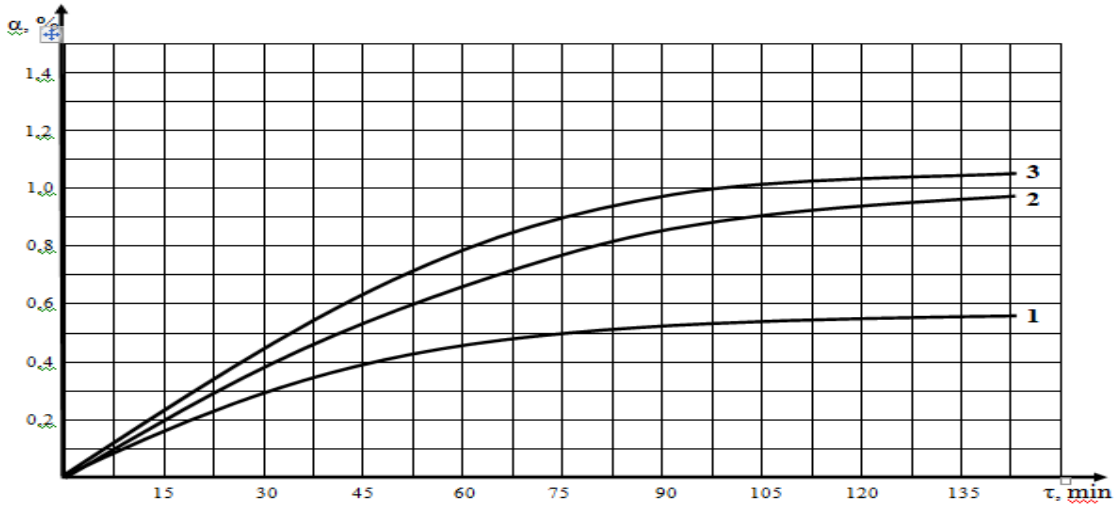

Figure – Dependance of the swelling degree in spirit-benzyl solution throughout time:
1) PhFO modified by oksamide; 2) PhFO modified by acetamide; 3) PhFO unmodified.

Table 2 – The main characteristics of sulphocationites on the basis of volume and modified PHFO

Sulphocationites	Functional group	Size of particles, mm	Bulk weight, g/ml	Swelling degree, %	Specific volume, ml/g	Static volume capacity, mg-ekv/g	Real density kg/m^3	Dynamic volume capacity mg-ekv/g
Sulphocationite on the basis of PHFO	$–SO_3$ –OH	0,8-2	0,708	0,25	3,0	2,10	1082,2	0,82
Sulphocationites on the basis of PHFO modified by acetamide	$–SO_3$ –OH >NH >CO	1-2	0,600	0,50	8,0	2,84	1188,6	0,98
Sulphocationites on the basis of PHFO modified by oksamide	$–SO_3$ –OH >NH >CO	1-2	0,52	0,15	8,4	3,62	1192	0,96

First an optimum amount of phenol-formaldehyde oligomer modified by acetamide and oksamide and sulphuric acid of 96% are fed into the reactor. The reactor is heated until oligomer is completely dissolved, then being dissolved, the solution is cooled up to room temperature. Then immediately 37% water solution of formaldehyde is fed into the cooled reaction mass. Later this reaction mass is put into a special tank located in an oil bath at 110ºC, where within 2 hours the solidification process goes on. After solidification the reaction mass is washed with water until it turns into clear water, then dried up and grained into 1-2 mm dimension particles [8].

Sulphocationites on the basis of modified by acetamide and oksamide-phenol-formaldehyde oligomers being the products of black colour are not dissolved in water and hydrocarbons.

The indices of the main characterristics of obtained sulphocationites have been researched (table 2).

It has been shown that as a result of presence of functional groups of various activity in the structure of sulphocationites on the basis of functionalized phenol-formaldehyde oligomers, their static capacity in comparison with sulphocationites on the basis of unmodified phenol-formaldehyde oligomers increases.

Though the density of sulphocationites obtained on the basis of modified PHFO rises, their swelling degree is higher, which is explained by partial dissolution of amide groups in water during the volume process. Increased dencity and corresponding decrease of bulk volume of sulphocationites on the basis of modified PHFO make easy regulation and their technical characterristics. Obtained sulphocationites have been used for softening the water of definite solidity.

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