

Polyfunctional Anion Exchangers on the Basis of Allyl Compounds, Glycidic Ethers of Dioxybenzenes and Some Di- and Polyamines

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Abstract

Scientific basis for preparation of new carbon-mineral adsorbents, supports, highly selective catalysts, and composite materials synthesized by a carbide cycle mechanism on the finely disperse particles of the iron subgroup metals, their alloys with some other metals is discussed. It was found that the carbide cycle mechanism involves the chemical and physical steps. The regularities of the process performance on the both stages are considered. Graphite filaments may be formed of graphite layers with either coaxial-cylindrical, coaxial-conic or stack orientations in the filament body. A number of primary and secondary properties of the graphite aggregates is being discussed. We have developed the methods for control the synthesis of carbon-mineral materials of the specified properties by varying the parameters of the metal particles, the nature of hydrocarbon decomposition, and the process mode.

Introduction

At present the synthesis of polymers on the basis of allylhalogenides, which are characterized by the significant chemical and thermal stability, is of considerable interest [1-3]. Owing to a combination of various allyl monomers with epoxy compounds the assortment of ion exchange resins, which raise sorption ability to ions of transient metals has been extended.

The study of reactivity of various vinyl monomers by the method of polarography is widely spread. In particular, polymerization kinetics of N-(2-vinyloxy)-ethylamine-N-(3-chloro-5,6-dicyan-1,4-benzoquinonile-2) has been investigated, the rate constants and activation energy of the process have been determined [4]. The optimal polymerization conditions of quinoid nitrogen-containing monomers on the basis of vinyl ether of monoethanolamine and allylamine have been found [5].

Kinetic peculiarity of free-radical polymerization of diallyl monomer on the basis of allylbromide and piperidine has been investigated [6]. The mechanism of intramolecular cyclization on pregelation stage of radical polymerization of diallyl ethers of isophthalic acid has been also investigated [7].

The purpose of the present work is the synthesis and investigation of the properties of polyfunctional anion exchangers on the basis of allyl bromide and chloride, diglycidyl ethers of resorcinol and hydroquinone, and also various amines (polyethylenepolyamine, polyethyleneimine, hexamethylenediamine), polarographic study of polycondensation kinetic of allylbromide, diglycidyl ether of resorcinol, polyamine and revealing of the reaction mechanism by the methods of elemental analysis, polarography, IR-spectroscopy.

Experimental

Dimethylformamide (DMF) was dried under calcium hydride and vacuum distilled at 44-45°/15 mm; n_D^{20} 1,4300 (b.p. 153°/760 mm) [8].

Epichlorohydrine (EchH) was dried under calcium hydride and overtook, selecting a fraction boiling at 115 -116°/689 mm; n_D^{20} 1,4380.

Allyl chloride (ACh) with n_D^{20} 1,4154 and b.p. 44,6°/760 mm as well as allyl bromide (ABr) with n_D^{20} 1,4655 and b. p. 71,3°/760 mm were used as received.

Polyethylenepolyamine (PEPA) was produced by Nizhne-Tagilsk factory of plastics. It was preliminary dehydrated by storage for a long time under granular

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KOH. The molecular weight of PEPA is 265 and n_D^{20} is equal to 1,1546. The contents of total nitrogen is 22%, the titrated nitrogen is equal to 19,1%.

Polyethyleneimine (PEI) with molecular weight 10^4 was used as 50% aqueous solution without further purification. The content of titrated nitrogen in an anhydrous PEI sample is 29,3%.

Hexamethylenediamine (HMDA) was «pure» grade with m.p. 42-43° and b.p. 204-205°.

Diglycidyl ethers of resorcinol (DER) and hydroquinone (DEH) were obtained by the method [9], and determination of epoxy groups was carried out as described in ref. [10].

The condensation of allylhalogenides (AHal) with the above-mentioned ethers and amines was carried out in the medium of DMF at the temperature of 13-24° during 0,5-2 h with a subsequent cure at 80-120°. The gel was crushed, scattered and a fraction with granules of 0,25 mm was selected for further experiments.

The static exchange capacity (SEC, mg-eq/g), moisture content, swelling capacity, chemical and thermal stability of the synthesized anion exchangers were determined by the standard techniques [11].

The polarographic studies were carried out on polarograph PU-1 with the characteristic of a capillary at the opening circuit $m^{2/3}t^{1/6} = 4,38 \text{ mg}^{2/3}\text{s}^{-1/2}$. The saturated calomel electrode was used as a reference. The polarographic studies were carried out on the background of 0,2 M LiCl and 0,02 M $(\text{C}_2\text{H}_5)_4\text{NI}$ in the presence of the solvents: 50% ethanol and 50% DMF.

The IR-spectra of initial, intermediate and final products were recorded, using a spectrophotometer SPECORD M 80/M 85 in tablets with KBr (200 mg KBr + 1mg of substance) and as a thin film between laminas.

Results and discussion

The structure and composition of diglycidyl ethers of resorcinol and hydroquinone have been identified by the IR-spectroscopy methods [12], as well as by the elemental and chemical analyses. The IR-spectroscopy data testify to the presence of bands responsible for absorption, characteristic for epoxy groups, in the range of 850-950, 1200-1250, 3000-3100 cm^{-1} . The content of epoxy groups in DER is 31,7 % and in DEH is 30,2 %.

In order to find the optimal conditions of the synthesis of anion exchangers the effect of initial components ratio, temperature conditions of prelimi-

nary condensation and solidity on some properties of anion exchangers have been investigated (Table 1).

It is seen that an increase of DGER concentration from 1 to 2,5 mass.parts results in the reduction of SEC from 8,9 to 5,9 mg-eq/g. The swelling of anion exchangers decreases from 9,3 to 5,2 mg/l, which is probably caused by an increase of cross-linking density. Upon an increase of the amine contents in the reaction mixture the formation of highly swelling or soluble polymers with the worsened physical-chemical properties is observed. For example, for anion exchanger on the basis of PEPA an increase of amine concentration from 1 to 2 mass. parts promotes a SEC increase from 6,5 to 9,9 mg-eq/g and swelling from 6,1 to 8,4 mg/l. An increase of PEI concentration from 1 to 3,5 mass. parts results in a SEC growth from 3,5 to 8,7 mg-eq/g. Upon the use of HMDA as an amination agent, its excess more than 1 mass.parts results in the formation of soluble products.

The influence of the temperature of preliminary condensation and solidity on SEC of anion exchangers has been investigated with optimum ratio of initial components (Table 2).

It has been found that with an increase of temperature of preliminary condensation from 13 to 24°C the exchanger capacity increases from 5,3 to 9,9 mg-eq/g. With an increase of solidity temperature from 80 to 120°C anion exchangers SEC decreases from 9,9 to 7,4 mg-eq/g, which is apparently caused by the rising of density of cross linking junction due to additional crosslinking of polymer chains because of disamination and degradation reactions.

The data on the influence of the nature of initial components on static exchange and sorption capacity of anion exchangers are summarized in Table 3.

According to the obtained results, the SEC values and anion exchangers sorption capacity relating to the ions of transient metals strongly depend on the nature of amines: the most effective is PEPA, the application of which allows to synthesize polymers with SEC 9,9; 10,2 mg-eq/g. The nature of allylhalogenides and diglycidyl ethers renders an insignificant influence on the studied characteristics. All exchangers have high sorption capacity in respect to the ions of nickel, cobalt and copper. The more efficient sorbents are anion exchangers on the basis of PEI and HMDA.

Thus, the optimal conditions for the synthesis of anion exchangers on the basis of allylhalogenides have been found to be as follows: the temperature of preliminary condensation is 24°C, the solidity temperature is 80°C, the duration - 2 h, the mass ratio

Table 1

Influence of ratio of initial components on SEC and swelling of anion exchangers

Ratio of initial components, mass. parts			SEC on 0,1N HCl, mg-eq/g	Swelling, ml/g
PEPA : ABr : DGER				
1.0	1.0	1.0	8.9	9.3
1.0	1.0	1.5	6.5	6.1
1.0	1.0	2.0	6.1	5.5
1.0	1.0	2.5	5.9	5.2
1.5	1.0	1.5	6.7	6.8
2.0	1.0	1.5	9.9	8.4
PEI : ABr : DGER				
1.0	1.0	1.5	3.5	2.4
1.5	1.0	1.5	5.4	2.9
2.0	1.0	1.5	5.9	3.1
2.5	1.0	1.5	6.2	3.4
3.0	1.0	1.5	7.1	3.8
3.0	1.0	1.5	8.7	4.1
HMDA : ABr : DGER				
0.5	1.0	1.5	3.6	3.2
1.0	1.0	1.5	5,1	4,4-diaminodiphenolmethane
1.5	1.0	1.5	soluble	-

Table 2

Influence of preliminary condensation and solidity temperature on SEC of anion exchangers

Anion exchanger	Preliminary condensation		Solidity	
	t, °C	SEC on 0,1N HCl, mg-eq/g	t, °C	SEC on 0,1N HCl, mg-eq/g
PEPA : Abr : DGER	13	5.3	80	9.9
	18	8.2	100	8.0
	25	9.9	120	7.4

PEPA : AHal : DGER = 2,0:2,0:1,5; PEI : AHal : DGER = 3,5:2,0:1; HMDA : AHal : DGER = 2:2:1,5.

An important parameter of anion exchangers is their chemical and thermal stability. It has been concluded that the chemical stability of anion exchangers has been estimated according to the change of exchange capacity in the solutions of 5N sulfuric acid, caustic soda and 10% H₂O₂. As it is seen from Table 4 the polymers on the basis of PEPA are less stable to the action of oxidizers and acids. The study of ther-

mal stability of the obtained anion exchangers in sealed ampoules at 100°C and duration 12 h. has shown that the loss of capacity does not exceed 8 %.

The polyfunctionality of anion exchangers has been confirmed by the method of potentiometric titration (Fig.1,2).

The interaction mechanism of allyl bromide, diglycidyl ether of rezorcinol ether with PEPA during anion exchangers synthesis has been investigated by the polarographic method, IR-spectroscopy and

Table 3

Influence of the nature of initial compounds on SEC and sorption capacity of anion exchangers

Anion exchanger	N, %	SEC on 0.1N HCl, mg-eq/g	Sorption capacity, mg-eq/g		
			Cu ²⁺	Ni ²⁺	Co ²⁺
PEPA : ABr : DGER	12.97	9.9	9.8	4.6	3.9
PEI : ABr : DGER	16.55	8.7	7.7	4.1	3.9
HMLA : ABr : DGER	9.56	5.0	5.0	3.5	3.1
PEPA : ACI : DGER	13.15	10.2	10.2	5.4	5.3
PEI : ACI : DGER	16.17	6.6	5.4	3.5	3.1
HMDA : ACI : DGER	9.98	5.1	5.0	2.9	2.3
PEPA : ABr : DGEH	11.02	8.9	8.6	4.0	3.6
PEI : ABr : DGEH	15.40	7.8	7.2	4.0	3.4
HMDA : ABr : DGEH	8.62	4.3	4.1	2.8	2.5

Table 4

Chemical and thermal stability of anion exchangers on the basis of allyl bromide, DGER and various amines

Amine	Chemical stability, %			Thermal stability, %			
	5N NaOH	5N H ₂ SO ₄	10% H ₂ O ₂	2 h	4 h	7 h	12 h
PEPA	100	94	90	100	99.6	94	92
PEI	100	100	90	100	100	98.8	96.5
HMLA	100	98	92	100	100	100	100
PEPA	100	92	89	100	100	98	98
PEI	100	100	91	100	100	98.6	98.6
HMLA	100	96	91	100	99.2	97.6	97.6

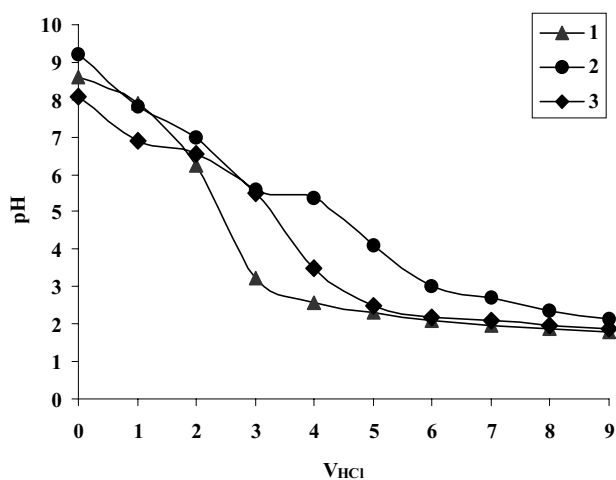


Fig. 1. Potentiometric titration curves of anion exchangers on the basis of PEPA:ABr:DGER (1), PEI:ABr:DGER (2), HMDA:ABr:DGER (3)

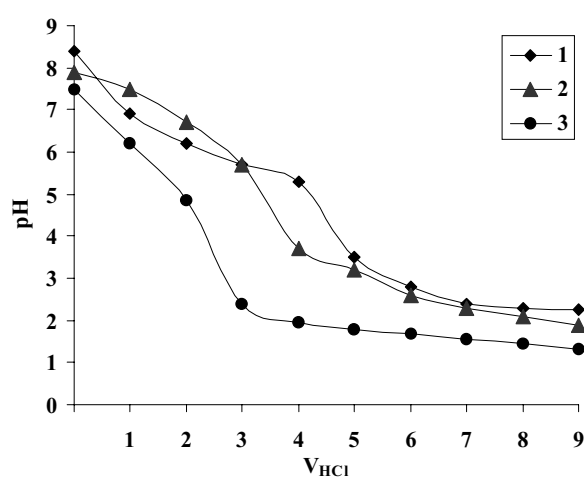


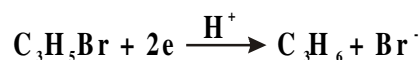
Fig. 2. Potentiometric titration curves of anion exchangers on the basis of PEPA:ACI:DGER (1), PEI:ACI:DGER (2), HMDA:ACI:DGER (3)

chemical analysis.

The polarographic qualitative determination of substances is based on the comparison of values of semi-wave potentials, which are characteristic and specific for separate compounds under certain conditions.

It has been determined [13,14], that the significant number of haloid - substituted organic compounds are capable to be reduced on mercury dropping electrode at the potential from 0 to -2,5 V. Two electrons are usually spent for electrochemical break of carbon –

halogen bond of monohaloid derivatives. Thus halogen is allocated as anion, and its place in an organic molecule is occupied by a hydrogen atom:



The process on current-voltage curves corresponds to the one-step two-electronic diffusion-limited waves (Fig.3).

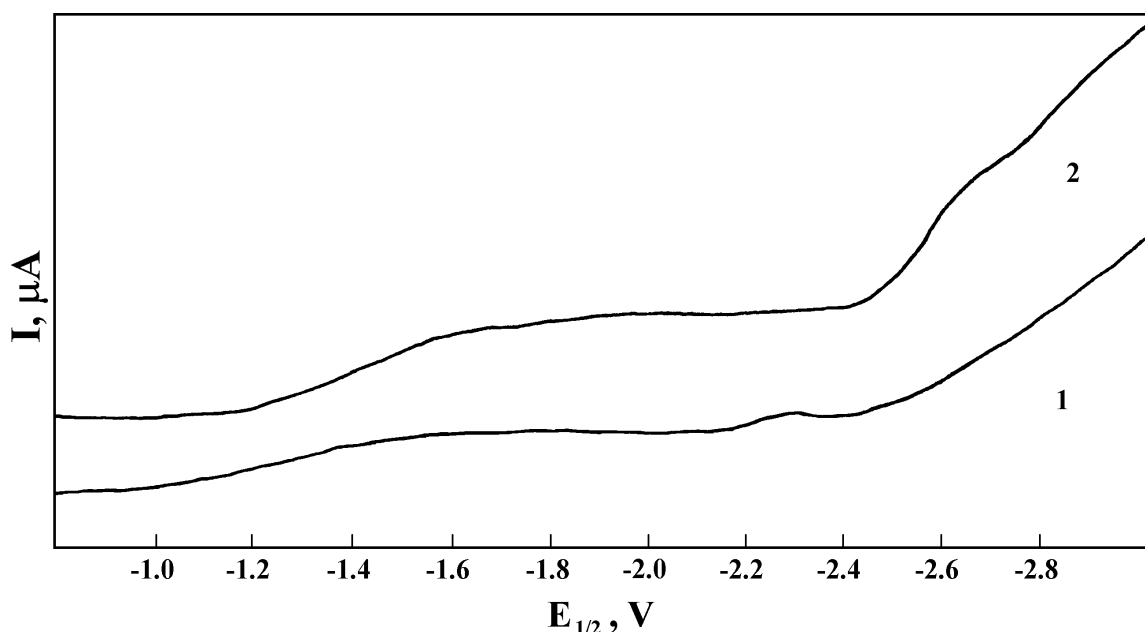


Fig. 3. Polarographic wave of allylbromide (1), allylbromide and DGER (2).

The potential of semi-wave $E_{1/2}$, characteristic for allylbromide reduction in 50% ethanol solution with a background of buffer solution (pH=5,45) and in 75% dioxane solution with a background 0,05 M $(\text{CH}_3)_4\text{NBr}$ is equal to -1,29 V [15].

We have investigated allylbromide reduction in 50% ethanol and DMF solutions with a background 0,2 M LiCl and 0,02 M $(\text{C}_2\text{H}_5)_4\text{NI}$. The data on the influence of the nature of the solvent and background on $E_{1/2}$ for allylbromide are presented in Table 5.

As it is seen from Table 5 the semi-wave potential $E_{1/2}$ of reduction of allylbromide with a background of 0,2 M LiCl is lower, than that with a background of 0,02 M $(\text{C}_2\text{H}_5)_4\text{NI}$. In order to record the current-voltage curves (Fig. 3) we have chosen a solution of 0,02 M $(\text{C}_2\text{H}_5)_4\text{NI}$ in 50% DMF as a background, because DMF is adsorbed very strongly on the surface of a mercury dropping electrode and hinders the

Table 5

Influence of the nature of the solvent and background on $E_{1/2}$ allylbromide reduction

Background	Solvent	$E_{1/2}$
0,2 M LiCl	50 % ethanol	- 1,23
	50 % DMF	- 1,21
	50 % ethanol	- 1,29
0,02 M $(\text{C}_2\text{H}_5)_4\text{NI}$	50 % DMF	- 1,29

appearance of polarographic maxima [16].

Upon addition of DGER to the reaction mixture containing allylbromide, the potential of semi-wave of allyl bromide reduction is displaced to the range of more negative values (from -1,29 to -1,39 V). It is connected, probably, with an increase of the molecules size, molecular weight of the substance and electron

density of chains. Here a positive induction effect of alkyl groups is observed to some extent. According to the Shikata-Tchi rule [17] an introduction of the substituents showing +I - effect into a molecule, displaces $E_{1/2}$ to the more negative values in comparison with electroreduction of the initial compound.

Polarographic method is used for the study of the ability of monomers to a polymerization reaction in accordance with the values of semi-wave potentials of these compounds. An investigation of the reduction of $-C=C-$ bond in allylbromide with a background of 0,02 M $(C_2H_5)_4NI$ in 50 % DMF has shown that an addition of DGER to Abr shifts semi-wave potential $E_{1/2}$ of the reduction of double bond to the more negative range from -2,22 to -2,56 V too. It can be explained by the fact that electronodonor substituent, which has replaced a Br atom in the initial allylbromide, increases the electronic density at double bond and results in difficulty of its polarographic reduction. It can be explained by the fact that the free electronic pairs $-O-$ atoms are displaced towards a double bond, raising the density of an electronic cloud. As a result, the reactivity of a radical grows, which is responsible for a homopolymerization rate.

In order to confirm the proposed mechanism we have recorded the IR-spectra of initial substance, carrier and the obtained compounds (Fig. 4). The displacement of absorption bands seen from the figure, characteristic for vibrations of a $C-Br$ bond and valency vibrations $C=C$ - bonds, to the range of the larger waves lengths (in the initial monomer for bond $C-Br$ - 500-600 cm^{-1} , $C=C$ - bond - 1640 cm^{-1} , in the formed intermediate substance accordingly - 664, 1680 cm^{-1}) can occur due to an increase in the size and weight of a molecule [18]. It shows that the initial allylbromide enters the reaction with DGER already at the first stage, which is confirmed by a disappearance of frequencies in the range of 850-1200 cm^{-1} , characteristic for the epoxy ring. The absence of absorption bands corresponding to the $C-Br$ in a spectrum of a final product confirms that the polycondensation of intermediate substance with amine takes place with an isolation of a low molecular product HBr .

The data of a possibility of double bond opening in an allyl group, investigated by the bromide-bromate method [19], are presented in Table 6.

The results of Table 6 show that in the process of allyl group bonding to a molecule of ether, a bromine number increases. After addition of PEPA it increases more than twice (from 5,5 to 13,1). It is probably due

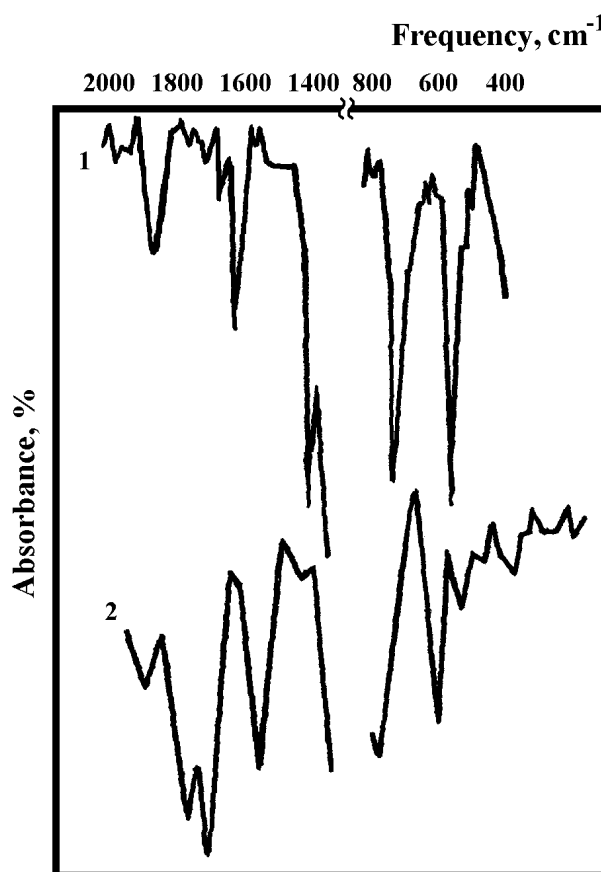


Fig.4. IR-spectra of allyl bromide (1) and its mixtures with DGER (2).

Table 6

Dependence of bromine number change on time

Stage	τ , min	Bromine number
ABr + DGER	5	2.6
	10	3.3
	30	3.9
	60	5.5
ABr + DGER + PEPA	5	13.1
	10	5.3
	30	6.9
	60	7.8

to an exothermic nature of the reaction mixture, which results in an intensification of the interaction between ABr and DGER. It promotes the double bond opening in an allyl group of the intermediate substance. This leads to a decrease of bromine number in subsequent 5 min. from 13,1 down to 5,3. Polarographic

studies have shown that the intermediate substance, due to an increase in the electronic density on a double bond, has the greater ability for homopolymerization, than that of the initial ABr. A further slow increase in a bromine number testifies to the fact that during the process of cooling of the reaction mixture, the opening of double bonds ceases. Then there is only a reaction of a CBr bond takes place. Upon solidification of the gel formed (80°-100°C) the probability of oligomers formation grows because of the opening of C=C - bonds.

Conclusion

Thus, by a condensation of the specified allyl-halogenides, diglycidic ethers of dioxybenzenes with various amines in DMF medium with subsequent gel solidification, the new polyfunctional anion exchangers with high exchange capacity and raised physical chemical characteristics have been obtained. The optimal conditions for the synthesis of anion exchangers have been found and some of their properties have been investigated. It has been established by methods of polarography, IR-spectroscopy and chemical analysis that the use of allylhalogenides allows to synthesize anion exchangers of a spatial structure not only due to cross-linking by amines, but also owing to the double bond in allyl group.

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