

## STUDY OF DETERMINATION OF STATIC EXCHANGE CAPACITY OF COMPLEX DERIVATIVE IONITES BY TITRIMETRIC METHOD

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**Abstract.** This article presents the determination of the static exchange capacity of complex forming ions using the method of titrimetric analysis. Based on the data obtained as a result of the study of the dependence of the sorption of some metal ions on various factors in the tested anionites, the optimal indicators of the sorption process were selected. It was also shown that in the process of sorption of copper ions, in addition to the industrial anionite AN-31, the anionite DMT+GIPAN obtained on the basis of local raw materials can be used.

**Keywords.** Local crude, ionite, metal ion, sorption, titrimetric, exchange, capacity.

**Introduction**

As industries expand and develop worldwide, the demand for ionites is increasing. Phenol, formaldehyde, epichlorohydrin, styrene, divinylbenzene, amino compounds and amides of various acids are used as the main raw materials in the production of ionites. In particular, thermopolymers based on salicylic acid, melamine and formaldehyde were obtained by the sopolycondensation method. Their ability to form complexes with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  ions was studied. The degree of sorption of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  ions in a wide range of pH is indicated [1].

As a result of the use of benzoyl peroxide initiator in the presence of glycidyl methacrylate and cellulose etching agent N,N'-methylenebisacrylamide, graft copolymerization of -NHR<sub>2</sub>CI functional group (AN) was obtained. Characterized by anion scavenger- IR-spectroscopy, scanning electron microscope, PV comparative analysis, TGA and potentiometric titration methods. It was concluded that it is a promising sorbent for separating vanadium from aqueous solutions [3].

Peat humic acids with an aromatic structure were modified with formaldehyde or paraform and then treated with hydrogen chloride or concentrated HCl in the presence of  $\text{ZnCl}_2$ . The sorption capacity of the obtained humic preparations (GP) was tested under static conditions at room temperature, in model solutions containing 0.001 M  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  cations, as well as in real effluents of the chemical industry. The degree of separation of metal cations of the modified GP was 12-78% higher than that of the original GP, and it was 25-100% [4].

Resins were obtained on the basis of 8-hydroxyquinoline-5-sulfo-acid-thiourea-formaldehyde copolymer formed by the condensation of 8-hydroxyquinoline-5-sulfo-acid and thiourea with formaldehyde in the presence of hydrochloric acid in different mole ratios of reacting monomers. Resins are selective to some metals. The chelating properties of these copolymers were studied for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  ions. Studies were performed in media of different ionic strength and over a wide range of pH. Copolymers have been shown to be more selective for  $\text{Fe}^{3+}$  ion than for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Pb}^{2+}$  ions [5,6].

Tertiary copolymers were obtained from the condensation of 2,4-dihydroxybenzophenone, oxamine and formaldehyde in different proportions in the presence of different amounts of acidic catalyst. The ion exchange properties of the obtained copolymers were studied and it was shown that compounds containing  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  metal ions can be effectively separated. Hydrochloric acid was used as a catalyst in

the polycondensation of the tertiary copolymer [7].

#### Material and Methods

**Materials.** To study the sorption ability of the synthesized mesh polymers to some metal ions, "k.t." aqueous solutions of branded salts were used.

Individual masses of ionites were transferred to the  $\text{OH}^-$  form, and the exchange capacity of ionites was determined using the potentiometric titration method at room temperature at a mass ratio of 1:100 of ionite:solution under static conditions. Different amounts (0-12 mg-eq/g) of solutions of copper sulfate, cobalt and nickel nitrate salts in 0.1 N sulfuric and nitric acids were poured into the sample of  $\text{OH}^-$  form ions weighing 0.2 g. Dry sodium nitrate or sulfate was added to bring the solution to an ionic strength of 1. After the formation of equilibrium (7-10 hours), the pH of the solution was determined in the meter "pH - 340" and the concentration of metal ions was determined by the trilonometric (atomic-absorption) method.

**Methods.** The concentration of the complex-forming metal in the equilibrium solution, the total amount of free, protonated amino groups bound to the complex, their degree of ionization, as well as Beerum's formation function were determined according to the method presented in [8]. The composition and stability of complex compounds formed by anionites with metals were calculated based on the following equation according to Beerum's modified method [9]:

$$\lg\beta_n = \lg K_{ycm} + \lg K_\alpha$$

The static exchange capacity was determined from the potentiometric titration curve according to the following formula:

$$COE_{nom} = \frac{B \cdot H}{\Gamma}$$

H - normality of acid solution, V - volume of acid solution, ml. G - ionite gravity, g.

Research of physico-chemical and mechanical properties of ion-exchange polymers allows to determine the fields of application of synthesized anionites. On the other hand, the physico-chemical study of ionizers allows to determine some properties of anionites by means of modification. For this purpose, the physico-chemical and mechanical properties of the received ion-machine polymers were studied.

#### Experimental part.

Special laws of ionization, which serve to justify the physicochemical properties of anionites obtained as a result of interactions of dimethylolthiourea with polyethylene polyamine, melamine, GIPAN and orthophosphoric acid, were studied. One of the main chemical properties of ionites of important practical importance is the ability to ionize, which allows to evaluate their operational properties. The size of the ion exchange capacity mainly depends on the amount of -ionite ionogenic groups, their degree of dissociation, their nature, and the concentration of exchangeable ions. The static exchange capacity is usually determined mainly in the presence of mineral acids (chloride, sulfate, nitrate) in the solution.

The kinetic equilibrium constants of the synthesized ionites were compared with the kinetic equilibrium constants of industrially used polycondensation ionites such as EDE-10P, AN-2F, AV-16 and AN-31 (Table 1).

**Table-1**

The main properties of tested ionites

Indicators, Ionites	Flexible weight	OH is the specific volume of the crushed ionite in the form	SAS, 0.1N HCl solution	CAC, 0,1N HNO <sub>3</sub> solution	CAC, 0,1 N H <sub>2</sub> SO <sub>4</sub> solution	Mechanical strength
Unit of measure	g/ml	g/ml	mg-eq/g	mg-eq/g	mg-eq/g	%
DMT+PEPA	0,60	2,2	4,3-4,5	4,0	4,1	99,7
DMT+M	0,65	3,6	6,0-6,5	5,4	5,8	99,7
DMT+HYPAN E	0,75	4,0	6,5-7	6,0	5,0	99,8
DMT+FK	0,40	2,0	4,2-4,4	3,9	4,2	97,9
EDE-10P	0,60	4-4,5	7,5	-	8,5	97,7
AN-31	0,55	3,2	3,7	-	7,5	99,8
AN-2F	0,55	4,5-5	6,2	-	6	-
AV-16	0,65	4,5	3,4	-	-	-

The dependence of the sorption capacity of the obtained ionites on the environment pH and the initial form of ionogenic groups was studied by potentiometric titration. The results are presented in Table 2 below.

The data presented in this table confirm that most of the tested ionites belong to the group of weak bases.

According to the potentiometric titration curves of ionites obtained on the basis of DGT+PEPA and DGT+M, absorption of metal ions into ionites occurs in weakly acidic environments. (Figure 1).

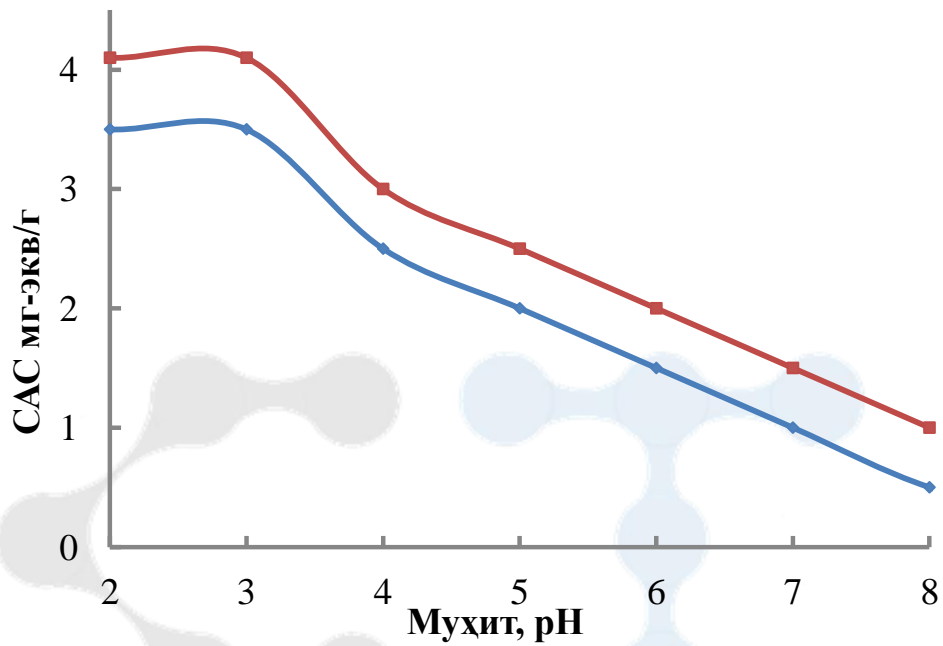
As can be seen from Figure 1, the characteristics of changes in the titration curves of OH<sup>-</sup> and SO<sub>4</sub><sup>-2</sup> ionites indicate that they are weakly basic.

The indicator of the dissociation constant of ionogenic groups was found from the titration curve according to the method [10].

Table-2.

The results of the potentiometric study of the obtained ionites

Ionites	CAC, 0,1 N HCl mg-eq/g in solution	AS by potentiometric titration curve, mg-eq/g		pK <sub>OH</sub>
		OH – form	SO <sub>4</sub> – form	
DMT+PEPA	4,3	4,0	4,3	9,0
DMT+M	6,0	5,6	3,1	8,2
DMT+HYPANE	6,5	6,1	2,8	8,0
DMT+FK	4,2	4,1	2,2	7,0
EDE-10P	5,5	4,2	4,5	-
AN-31	3,7	3,2	4,2	-
AN-2F	6	2,1	3,9	-
AV-16	3,4	3,2	4,0	-

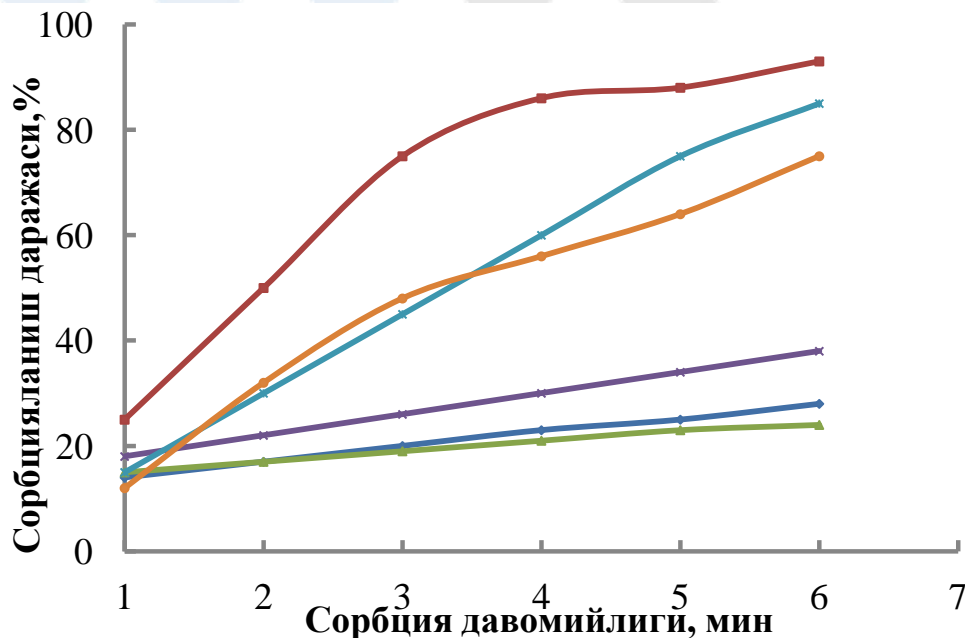


1) DMT+PEPA – OH<sup>-</sup> (—◆—); 2) DMT+PEPA SO<sub>4</sub><sup>2-</sup> (—■—).

**Figure 1. Dependence of ion exchange capacity on medium Ph**

As shown in Fig. 1, according to the characteristic of the curve, the exchange capacity of ions increases from a small value of rN, and the mutual comparison of the curves at rN 2.0-3.5 showed that the nature of the ionite saturated metal ion affects the characteristic of the titration curve. As the total exchange capacity decreases, it approaches the ordinate axis. The points obtained in the experiment are close to each other on the curve.

The ionogenic groups in the obtained anionites were studied using IR spectra and their structure was determined.



1. АВ-16- SO<sub>4</sub><sup>2-</sup> (—◆—); 2) АВ-16 NO<sub>3</sub><sup>-</sup> (—■—); 3) АВ-16 Cl<sup>-</sup> (—▲—); 4) ДГТ+ПЭПА SO<sub>4</sub><sup>2-</sup> (—×—); 5) ДМТ+ПЭПА NO<sub>3</sub><sup>-</sup> (—\*—); 6) ДМТ+ПЭПА Cl<sup>-</sup> (—○—).

**Figure 2. The rate of ion sorption in ionites**

In addition to ionization capacity of ionites, the rate of ionization - the kinetics of the process is also of great practical importance. The rate of sorption of acid ions in the resulting ions is 0.1 n. from solutions of sulfuric, nitric and hydrochloric acids were studied under static



conditions. The obtained results were compared with the properties of AV-16 ionite. Figure 4.2 shows the experimental results in F-t coordinates. F is the level of reaching equilibrium; %, t – duration of sorption, hours [11].

Figure 2 shows that the DMT+PEPA ionite absorbs the tested ions faster. AV-16 shows a slightly lower kinetic property under these conditions.

Ion-exchange polymers undergo rapid changes in industrial conditions: air, water, aqueous solutions of acids, alkalis and thermal effects. A comprehensive study of the thermal stability of ionites allows to determine a comfortable temperature limit in the state of thermal stability, which is satisfactory for use at high temperatures. Almost all anions are more or less thermally unstable.

Ionites	Indicators					
	CAC mg-eq/g		ДAC mg-eq/g		Water solubility, ml/g	Soluble weight, g/ml
	0,1 H H <sub>2</sub> SO <sub>4</sub>	0,1 H HCl	0,001 H NaCl	0,1 H NaOH		
DMT+PEPA	4 -4,5	4-4,5	200-250	250-280	1,73-2	0,6 - 0,7
DMT+M	5,8-6	6,5-7	200-220	230-260	1,5-1,7	0,6 - 0,7
DMT+HYPANE	4,5-5	7-7,5	300-350	330-370	3,2	0,6 - 0,7
EDE-10P	8,5	7,5	200-220	220-250	4-4,5	0,6 - 0,7

Table 3 lists the main ionization characteristics of the polyfunctional ionites synthesized on the basis of DMT, as well as the industrial ionite EDE-10P.

Based on the obtained results, there was interest in comparing the synthesized DMT+PEPA anionite and AN-2F, EDE-10P industrial anionite in terms of thermal stability. The ON-form of anionites was used in this. Thermal stability was determined by changes in anionite exchange capacity, mass, and specific volume.

#### Conclusion.

Thus, based on the data obtained as a result of the study of the dependence of the sorption of certain metal ions on various factors in the tested anionites, the optimal parameters for conducting the sorption process were selected. It was also shown that in the process of sorption of some metal ions, along with the industrial anionite AN-31, the anionite DMT+PEPA obtained on the basis of local raw materials can be used. In addition, the sorption rate was tested on DMT+GIPAN ionite in addition to DMT+PEPA ionite. These polymer ions were obtained by modifying the hydrophilic molecules of GIPAN with various binders. The macromolecules of these polymer ionites consist of polar links, and the solubility of the synthesized ionite depends on the solution ionic strength.

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