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RESEARCH OF PROPERTIES OF POLYCONDENSATION TYPE PHOSPHORIC ACID CATIONIC EXCHANGE RESINS

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Abstract: *One of the main properties of ion exchangers is their exchange capacity. Static exchange capacity of the new phosphorus acid cationic exchange resins obtained by phospholysis of polymer based on cube waste of the Shurtan gas chemical complex and a secondary product of hydrolysis industry - furfural was determined by alkalometric titration using 0.1 N solution of NaOH and NaCl, capacity by phosphorus content in ionite and capacity by curves of potentiometric titration. The values of exchange capacity found by the above methods are almost indistinguishable from each other. The cationite belongs to moderately acidic ions, the found values of pK (apparent dissociation constants) indicate that the cationite has two functional groups that allow it to work in neutral, weakly alkaline and alkaline environments. The paper also found the dynamic capacity of cationite for 0.1 N CaCl₂ solution. The studies showed that the tested phosphoric acid cationite has good static and dynamic capacitance.*

Keywords: *ionite, furfural, polycondensation, ionogenic group, phosphorus cationite, cube residue, ion exchange.*

INTRODUCTION. Ion-exchange polymers are widely used in various fields of science and technology. In this regard, the requirements imposed by industry on the ion exchange resins with respect to thermal and chemical resistance; mechanical strength and selectivity are increasing. Many of these requirements are no longer satisfied by such universal ion-exchange polymers as KU-2, KU-1, SHS, etc., despite the fact that they have high indicators of kinetic and sorption properties [1]. Phosphorus-containing ion-exchangers occupy a special place among the known ion-exchangers from the physicochemical point of view [2]. These ion-exchangers have a number of valuable properties: high selectivity, thermal stability, mechanical strength, etc. [3]. The above properties determine the prospects of application of these ion-exchangers in various fields of national economy and industry. Ionites with phosphorus-containing groups represent a class of selective sorbents capable of displaying both selective and complex-forming properties. Phosphoric acid cations are characterized by the presence of three functional groups, two acidic hydroxyls and phosphoryl oxygen. In weakly acidic and alkaline media in the absence of complexing metals, they are characterized by the usual dissociation with cation exchange. The rate of exchange reactions for monovalent and divalent ions on phosphate cations is less than on sulfocation cations, the rate changes from strongly dissociating to weakly dissociating.

METHODS. Based on the above, we obtained phosphorylation of polymer obtained by polycondensation of cube wastes of Shurtan gas chemical complex with secondary raw materials of hydrolysis industry - furfuryol phosphoric acid cationite [4].

One of the main properties of ion-exchange polymers is the exchange capacity, which characterizes their performance properties.

The statistical exchange capacity (EC) of the sodium ion cationite obtained was determined from 0.1N solutions of NaOH and NaCl. Since the exchange capacity of phosphorus cationic exchange depends on the pH of the medium and the initial ionic form of the ion exchange resin, we investigated the sorption capacity of the cationic exchange resin by Ca^{2+} ions in H^+ and Na^+ - form. Exchange capacity of anion exchanger for 0.1 N NaOH solution was determined as follows:

The cationite was used in H-form.

1 gr of cationite was poured into 100 ml of 0.1 N NaOH solution, the duration of phase contact was three days. After three days, 10 ml was taken from this solution and titrated with 0.1 N HCl solution.

$$V_1 * N_1 = V_2 * N_2$$

V_1 – NaOH aliquot solution - 10 ml

V_2 – HCl solution used to titrate 10 ml of NaOH

N_1 – NaOH normality

N_2 – HCl normality

C_{init} – initial concentration of NaOH solution, mg-eq,

$$C_{\text{sol}} = 10 \text{ mg-eq}/100 \text{ ml NaOH solution}$$

C_{eq} – NaOH concentration after contact with the anionite, mg-eq,

$$10 \text{ mg } 0.1 = 3.8 * 0.1$$

$C_{\text{eq}} = 3.8 \text{ mg-eq}/100 \text{ mg NaOH solution}$

m – amount of mg-eq NaOH sorbed by the anionite (cation exchange capacity) by 0.1 N NaOH solution

$m = 10 \text{ mg-eq/g} - 3.8 \text{ mg-eq/g} = 6.2 \text{ mg-eq/g}$.

$m = 6.2 \text{ mg-eq/g}$ is the amount of mg-eq/g NaOH absorbed by 1 gram of cationic acid.

The theoretical exchange capacity (TEC) of the anionite was calculated according to Gelferich [3]:

$$\text{TEC} = \frac{1000}{a}, \text{ mg - eq/gr}$$

Where, a - the molecular mass of the elementary link of the cationic exchange resin.

The exchange capacity of the anion exchanger by the percentage of phosphorus in the cationic structure was determined by the formula:

$$E_{\text{theor}} = \frac{P_{\text{prac}} \cdot U_{\text{theor}} \cdot 12 \cdot 26}{P_{\text{theor}} \cdot 2} \text{ mg-eq/gr}$$

E_{theor} - is the calculated theoretical exchange capacityg - eq/g.

P_{theor} - theoretical content of P (phosphorus) in %.

R_{prac} - practical content of P (phosphorus) in ionite, %

RESULTS. Table 1 shows the values of exchange capacity of cationic exchange resins found by different methods.

Table 1.

The value of the exchange capacity of the obtained phosphorus cationic acid

| Cationic ion group | Exchange capacity mg-eq/gr | | | | | | | | |
|---|----------------------------|------------------------------|---|-----------------------------|----------------------------|--------------------------------|-----------------------------------|-----------------|-----------------|
| | P content, weight, % | According to titration curve | Calculations on the phosphorus content of the polymer | 0.1 N NaOH solution, H-form | 0.1N NaCl solution. H-form | 0,1N CaCl ₂ Na-form | 0.1 N MgSO ₄ , Ca-form | pK ₁ | pK ₂ |
| $\text{R}-\text{P} \begin{matrix} \text{OH} \\ \text{=O} \\ \text{OH} \end{matrix}$ | 16 | 7.5-8.2 | 7.8-8.0 | 7.5-7.8 | 7.8-8.0 | 3.2-3.5 | 2.8-3.2 | 3.5-3.8 | 7.5-7.8 |

where **R** - is a macromolecule of the cationic polymer framework.

The data in Table 1 shows that the value of the exchange capacity found on the titration curve calculated from the percentage of phosphorus in the polymer structure is almost the same as the static exchange capacity for 0.1N NaOH solution.

The influence of the pH of the medium on the value of the exchange capacity was studied by the method of potentiometric titration proposed by Grissbach, which allows a fairly complete characterization of the ionite Fig. 1[4].

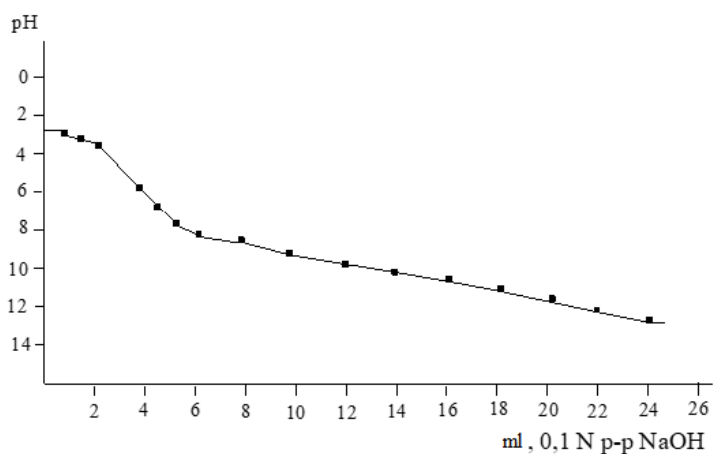


Figure 1. Potentiometric titration curve of phosphorus cationite

The curve obtained allows to characterize the ion-exchanger on the one hand by its capacity and on the other hand by its acidity and thus allows to estimate the working interval of the ion-exchanger. The curve of potentiometric titration shows that the cation exchange resin is polyfunctional, the complete ionic dissociation of active groups occurs at pH=8÷10.

The curve capacity of the ion-exchange resin was calculated from the intersection point of the titration curve and the line parallel to the abscissa line passing through pH=7 or, even better, from the inflection point of the curve. For this purpose a line parallel to the abscissa axis was drawn through the inflection point of the curve, the distance was divided in half. The vertical line

drawn through this point crosses the pH curve at the point where $\text{pH}=\text{pK}$. The titration curve of cationic exchange resins has two kinks, indicating the presence of two functional groups with different degrees of dissociation in the structure of the ion-exchange resin. The value of exchange capacity, according to elemental analysis, calculated from the phosphorus content in the polymer and the titration curve is higher than the value of static exchange capacity determined by the standard method (Table 1). The increase in the exchange capacity during potentiometric titration is caused by the influence of the addition of the neutral salt NaCl during titration. From the results of potentiometric study to characterize the cationite by its degree of acidity, we calculated the values of pK_{dis} (apparent dissociation constant) of the active groups according to the Henderson Hasselbach equation [5]

$$\text{pH} = \text{pK} - \text{nlg} \frac{1-\alpha}{\alpha}$$

where α - degree of dissociation of cationic active groups.

The degree of dissociation of the active groups in the ion can be calculated as follows:

$$\alpha = \frac{\text{exchangecapacityofthepotentiometrictitrationcurves}}{\text{fullexchangecapacity}}$$

Total exchange capacity calculated from the content of phosphorus in the ion-exchange resin (P in %). Apparent dissociation constants (pK) of ionogenic groups found from the titration curves by the above method correspond to $\text{pK}_1 = 3.5 - 3.8$, $\text{pK}_2 = 7.5 - 7.8$ (Table 1) [3].

The results show that the tested cationite is able to exchange ions in weakly alkaline, neutral and alkaline media.

Considering that ion-exchange processes in industry are carried out under dynamic conditions, we determined the dynamic exchange capacity of the cationic exchange resins obtained. For this purpose, 0.1 N CaCl_2 solution was passed through 100 ml of swollen cationite in H-form, with a grain diameter of 0.5 mm. The cationite was placed in a column with a diameter of 5 cm. In the samples passed through the cationic-exchange capacity before the CaCl_2 concentration equalization before contact with the cationite and after contact with the cationic-exchange resin was constantly determined according to the formula:

$$\text{ODCC} = \mathbf{a * (n - c) * 10 \text{ mg-eq/l}}$$

where, ODCC – operating dynamic capacity of the cationic-exchanger.

a - initial concentration of CaCl_2 , mg-eq/l.

n - the amount of CaCl_2 passed through the cationic-exchanger layer before slipping, ml.

c - amount of water displaced from the CaCl_2 solution filtrate (the amount of water contained in the cationic-exchanger layer is calculated on the basis of specific volume of swollen cationic-exchanger, the volume of water under the filtering bottom is added to the obtained value).

$$\text{TDCC} = \mathbf{[a * (n - c) - \Sigma a_m]10}$$

where, TDCC - is the total dynamic capacity of cationic exchange resins, mg-eq/l.

n - number of ml of CaCl_2 passed through the cationic-exchanger layer before its saturation, liter.

a_m - amount of ml CaCl_2 in each portion of the filtrate after slurry, mg-eq.

The results of the research are shown in Table 2.

Table 2.

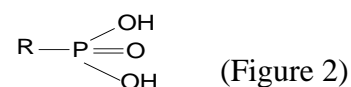
Data on one cycle of dynamic cationic capacity

| № | V ml of filtrate with 0.1 N CaCl_2 solution $k=1.0$ gr | Quantity ml of 0.1N Trilon B solution used to titrate the filtrate | Regeneration of cationic exchange resins with 5% HCl solution | | Washing with saturated NaCl solution of cationic exchange resins to neutral reaction |
|-----|---|--|---|----------------|--|
| | | | Vml of filtrate | Neutralization | |
| 1. | 500 | 8,0 | 250 | 6,8 | 250 |
| 2. | 500 | 9,05 | 100 | 13,7 | 250 |
| 3. | 500 | 9,05 | 100 | 14,0 | 250 |
| 4. | 500 | 9,05 | 100 | 14,0 | 250 |
| 5. | 500 | 9,05 | | | 250 |
| 6. | 500 | 9,05 | | | |
| 7. | 250 | 9,0 | | | |
| 8. | 250 | 8,5 | It took 500 ml of 5% HCl solution to regenerate | | It took 2,000 ml of discharged water to flush the cationic-exchanger |
| 9. | 250 | 6,75 | | | |
| 10. | 450 | 4,8 | | | |
| 11. | 250 | 2,8 | | | |
| 12. | 250 | 2,0 | | | |
| 13. | 250 | 1,6 | | | |
| 14. | 250 | 1,4 | | | |
| 15. | 250 | 1,25 | | | |
| 16. | 250 | 1,15 | | | |
| 17. | 250 | 1,15 | | | |
| | $\text{ODCC} = 324 \frac{\text{mg-nv}}{\text{l}}$ $\text{TDCC} = 420 \frac{\text{mg-nv}}{\text{l}}$ | | | | |

The results of determining the dynamic capacity, indicate that the synthesized cationite has sufficiently good sorption properties in the dynamics. We carried out 17 cycles specified in table 2. At the same time dynamic capacity and granulometric composition of cationite did not change. This indicates that cationite is characterized by sufficiently high mechanical strength.

The presence of ionogenic groups in the structure of the obtained cationic exchange resins was also studied by infrared spectroscopy. Thus, in the spectrum of phosphorus-acid cationite there are absorption bands in the region of 750 cm^{-1} corresponding to the carbon-phosphorus bond (**P-C**), i.e. to **P(OH)₂** group, absorption bands of oxidized cationite in the region of $1300-1250 \text{ cm}^{-1}$ correspond to **P=O** bond.

The absorption bands at 2560 cm^{-1} correspond to



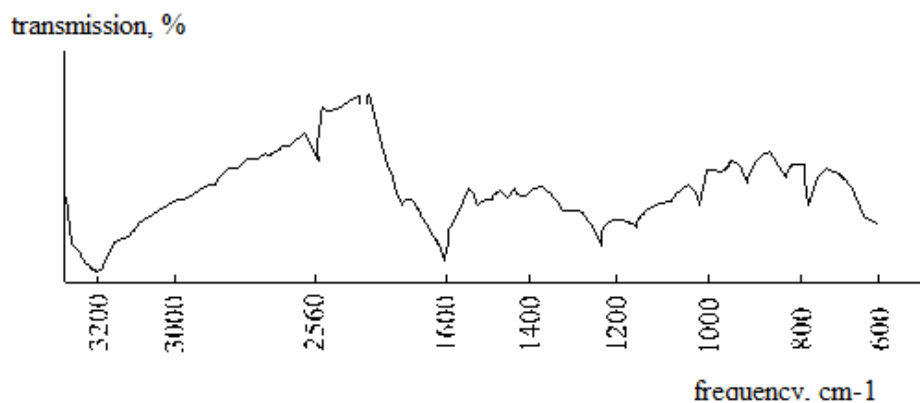
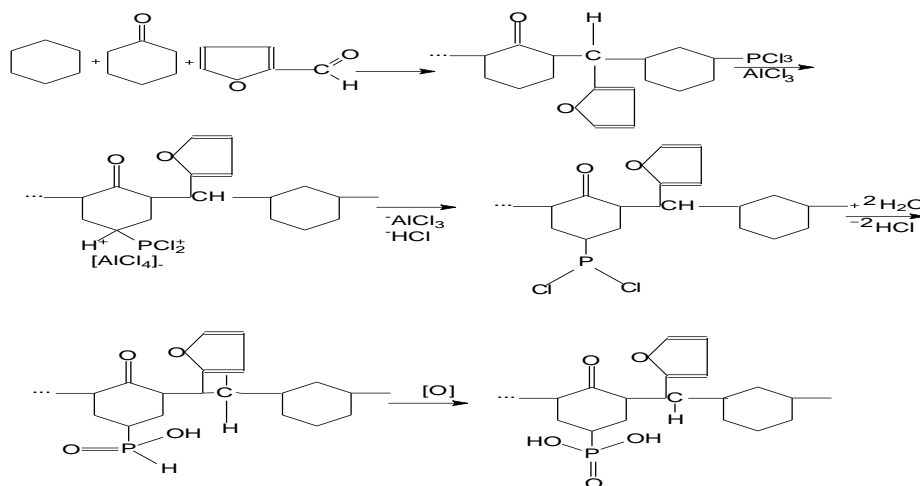


Fig.2. IR spectrum of the obtained phosphorus cationite (H-form)

Thus, based on the results of chemical analysis using physico-chemical methods of analysis: potentiometric titration, IR - spectroscopic analysis, the proposed structure of the polymer and phosphorus cationic exchange resins based on it was established.



Structure of the resulting polymer and the phosphate-based cationic exchange resin

Therefore, on the basis of the study it follows that the cationite we obtained has good exchange capacity both in static and dynamic conditions.

References:

- [1] Samsonov G.V., Trostyanskaya E.B., Elkin G.E. "Ionic Exchange" "Sorption of Organic Substances" Leningrad, "Nauka", 1969, pp 148-160.
- [2] Sinyavskiy V.G. "Selective Ionites" Kazan, Publishing House, 1967, pp 85-88.
- [3] Gelderich F. "Ionites" Moscow, IL 1962, pp 54-58.
- [4] Makhmudov Kh.A., Tursunov T.T., Nazirova R.A., Yuldashev A.A. Production of polycondensation cationite based on waste from chemical productions. Euro Asia 8th international congress on applied sciences. 2021, pp 249-250.
- [5] Grissbach R. "Theory and Practice of Ion Exchange" Publishing House, Moscow 1963, pp 70-75.

- [6] Sharipova U.I., Nazirova R.A., Pulatov Kh.L. (2019) Study properties of phosphate cation exchanger. *International Journal of Advanced Research in Science Engineering and Technology*, 12, 56-59.
- [7] Yuldashev A.A., Igitov F.B., Tursunov T.T., Pulatov Kh.L., Nazirova R.A., Azimov D.M. (2020) Obtaining of polycondensation type anion-exchange polymer// *Journal of Advanced research in dynamical and control systems*, Special issue, 7, 2125-2132.
- [8] Yuldashev A.A., Mutalov Sh.A., Pulatov Kh.L., Tursunov T.T., Nazirova R.A., Choriev R.E. (2020) Sorption of molybdenum ions by anion exchangers of polycondensation type. *Composition materials*, Special issue, 160-162.
- [9] Yuldashev A.A., Mutalov S.A., Nazirova R.A., Tursunov T.T., Azimov D.M. (2018) Weakly basic anion-exchange polymers. *Kimyo va kimyo texnologiyasi*, 2, 31-33.
- [10] Yuldashev A.A., Mutalov Sh.A., Pulatov Kh.L., Tursunov T.T., Nazirova R.A. (2020) Polycondensation anion-exchange polymers. *Science and education*, 1, 25-34.
- [11] Patent of RUz IAP 20100305 (2011) Method for producing of sulfocatianite/ Turobjonov S.M., Berdieva M.I., Mutalov Sh.A., Pulatov Kh.L., Tursunov T.T., Nazirova R.A., Abdutalipova N.A.
- [12] Vignoli Claudio Nogueira, Baé Jackeline M.C.F., Marques Monica R.C. (2015) Evaluation of ion exchange resins for removal and recuperation of ammonium-nitrogen generated by the evaporation of landfill leachate. *Polym.Bull.*, 12, 3119-3134.
- [13] Sharipova U.I., Pulatov H.L., Nazirova R.A., Kedeldaev B. (2019) Physicochemical properties of phosphate cation exchanger // *Technical sciences va innovation*, 4, 94-99.
- [14] Kekesi T. (2001) Anion-Exchange Separation in Hydrochloric Acid Solutions for the Ultrahigh Purification of Cobalt. *Metallurgical and Materials Transactions B. Process Metallurgy and Materials Processing Science*, 32, 4, 573-582.
- [15] Turobjonov S.M., Pulatov Kh.L., Tursunov T.T., Sharipova U.I., Nazirova R.A. Investigation of sorption and desorption of some ions by phosphate cation exchanger // *Composite materials*, 2010. - №2. - S. 38-41.
- [16] Yamabe Kazunori, Ihara Toshihiro, Jyo Akinori. Selectivity to metal ions of chelated cation exchangers containing phosphonium groups associated with phenyl residues of matrices based on styrene and divinylbenzene copolymers // *Separ. Sci. and Technol.*, 2001. - No. 15. - T.36. - S. 3511-3528.
- [17] Tiihonen Jari, Peuha Eeva-Liisa, Latva-Kokko Marko, Silander Sirpa, Paatero Erkki. Water as an eluent for chromatographic separation of carbohydrates using ion exchangers // *Separ. and Purif. Technol.* 2005. - No. 2. - T.44 - S.166-174.
- [18] Xue S. S., Gula M. J., Harvey J. T., Horwitz E. P. Control over the iron content in an electrolyte containing copper in the presence of a monophosphonosulfone-containing sorbent // *Miner. and Met. Process*, 2001. - No. 3. - T.18. - S.133-137
- [19] I-Hsien Lee, Yu-Chung Kuan, Jia-Ming Chern, Equilibrium and kinetics of heavy metal ion exchange // *Journal of the Chinese Institute of Chemical Engineers*. - 2007. vol. 38. - p. 71 - 84.
- [20] Erol Pehlivan, Turkan Altun, Ion-exchange of Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Ni^{2+} ions from aqueous solution by Lewatit CNP 80 // *Journal of Hazardous Materials*. - 2007. vol - 140. p. 299 - 307.
- [21] Horwitz E. P., Alexandratos S. D., Gatrone R. C., Chiarizia R. Ionites based on phosphonic acid. // *Eur. Polym. J.*, 2000. - No. 1. - T.40. - S.1215-1220.