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Research Article

Research Of The Reaction Of Polymers Phospholation Obtained On The Basis Of Waste Of Chemical Production

Makhmudov H[1], Turobjonov S.M.[2], Nazirova R.A.[3], Berdieva M.I.[4], Tursunov T.T.[5], Yuldashev A.A.[6], Gapparova Z.X.[7]

[1]Tashkent chemical-technological institute 100011, Republic of Uzbekistan, Tashkent city, Navoiy street, 32
[2]Tashkent state technical university, 100095, Republic of Uzbekistan, Tashkent city, University street, 2
[3]Tashkent chemical-technological institute 100011, Republic of Uzbekistan, Tashkent city, Navoiy street, 32
[4]Tashkent chemical-technological institute 100011, Republic of Uzbekistan, Tashkent city, Navoiy street, 32
[5]Tashkent chemical-technological institute 100011, Republic of Uzbekistan, Tashkent city, Navoiy street, 32
[6]Tashkent chemical-technological institute 100011, Republic of Uzbekistan, Tashkent city, Navoiy street, 32
[7]Tashkent chemical-technological institute 100011, Republic of Uzbekistan, Tashkent city, Navoiy street, 32

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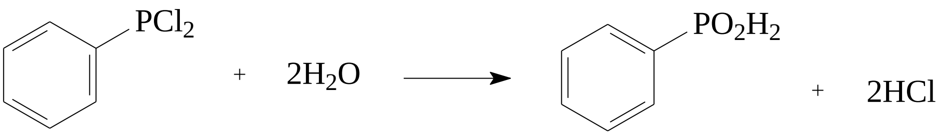
Abstract: Ion exchange polymers are widely used in various fields of science and technology. In this regard, the requirements made by the industry for their thermo-chemical resistance, mechanical strength and selectivity are increasing. Such universal ion-exchange resins as KU-2, KU-1, SHS, etc. no longer meet many of these requirements. Despite the fact that they have high kinetic and sorption properties [1]. Phosphorus-containing ion exchangers [2] have a special place among the known ion exchangers from a physicochemical point of view. These ion exchangers have a number of valuable properties: high selectivity, heat resistance, mechanical strength, etc. [3] These properties determine the prospects for the use of these ion exchangers in various areas of the national economy and industry. Based on the foregoing, by phosphorilation the polymer obtained by polycondensation of bottoms waste of the Shurtan gas chemical complex with the secondary raw material of the hydrolysis industry with furfural, we obtained a phosphate cation exchanger. [3].

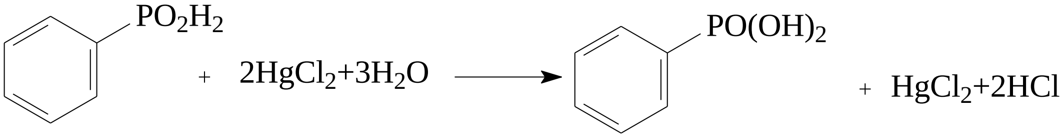
1. Phosphorylation of polymer based on still waste and furfural

The conditions for the phosphorylation of the polymer were selected from the experiments accumulated in relation to the phosphorylation of low and high molecular weight compounds. Michaelis, who obtained phosphenyl chloride by heating benzene with phosphorus trichloride in the presence of aluminum chloride in a stream of carbon dioxide for 36 hours, investigated the interaction of benzene with phosphorus trichloride in the presence of aluminum chloride. G.S.Kosolapov later found that phosphorylation of benzene derivatives can be carried out in the presence of Friedel-Crafts catalysts by heating the reaction mixture for 2-8 hours, using 2-3 moles of aluminum chloride per the amount of phosphorylated compound. By decomposition of phosphenyl chloride with water, phenylphosphorous acid was obtained, which, as a monobasic acid, readily forms the corresponding salts, for example: $C_6H_5PO_2NK{\cdot}2H_2O$; $C_6H_5PO_2HNa{\cdot}2H2O$ and others [5]. Investigating the structure of phenylphosphinic acid by the action of phosphorus pentachloride on it, Michaelis found that phenylphosphinic acid has an asymmetric structure, i.e. contains pentavalent phosphorus [5].



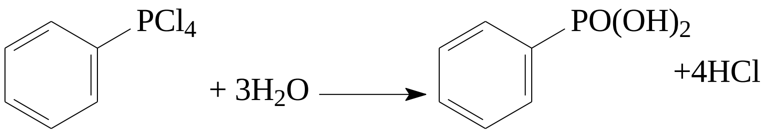
(1)

Phenylphosphinic acid under the action of some oxidants (O_2, $HgCl_2$, HNO_3, etc.) is cchanged into phenylphosphinic. For example, when $HgCl_2$ is used as oxidizing agents, the reaction proceeds according to the following scheme [6].



(2)

Phenylphosphinic acid can be obtained by other methods [5]. So, when acting on phosphenyl chloride, upon cooling, the phosphenyl tetrachloride is formed, which, as a result of hydrolysis, turns into phenylphosphinic acid.



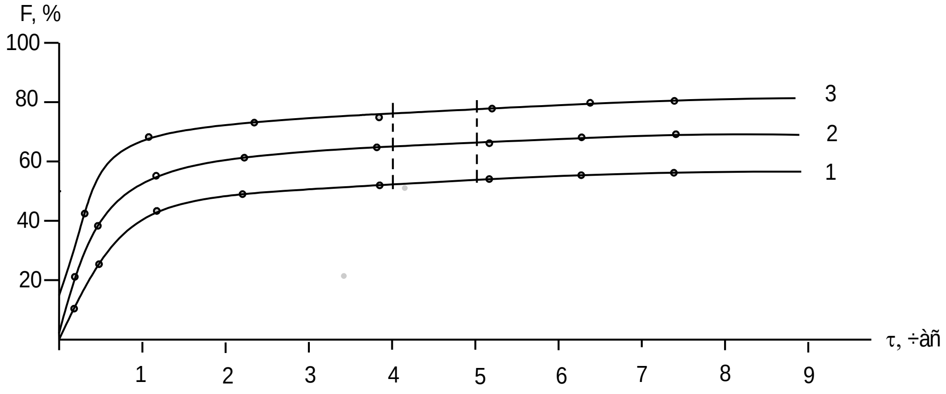
(3)

This method is impractical for phosphrylation of insoluble polymers, since the diffusion of chlorine deep into the insoluble polymer occurs very slowly. Thus, based on the foregoing, it follows that for the phosphorylation of high-molecular-weight compounds, the Mikhielis reaction should be used, while establishing the optimal conditions for the phospholization reaction in relation to polymers of three-dimensional structure. When phosphoric acid cation exchangers are obtained by the method of chemical or polymer-analogous transformations, the introduction of phosphoric acid groups and the polymer matrix can be carried out in several ways: - preliminary phosphorylation of the starting material followed by polycondensation from furfural;

- phosphorylation of the forecondensate;
- phosphorylation of the cured polymer;
- phosphorylation of polymer based on KO-1 and furfural.

A large number of works have been devoted to the reactions of polymer-analogous transformations of various polymers in order to obtain ion exchangers, in which the authors investigate the influence of the reaction duration, the concentration of the catalyst of the phosphorylating agent on the degree of polymer conversion [7, 8].There have appeared works devoted to the study of the kinetics of the reaction of polymeranological transformations in order to clarify the reaction mechanism and the limiting stage of the entire process of chemical transformations as a whole [9, 10]. In search of a convenient method for carrying out the reaction of phosphorylation of the synthesized polymer, the reaction was carried out in a medium of sophorictrichloride in the presence of aluminum chloride at 60 ° C, 70 ° C, 80 ° C. To study the change in the rate of the phosphorylation process, the dependences of the degree of conversion on time and temperature were taken. The kinetic curves were determined by the content of the introduced phosphorus and the static exchange capacity of the final product in a sodium hydroxide solution.

Figures 1, 2 show the kinetic curves, which were calculated using the known dependences of the reaction rate on time –Ig (1 - F) = k film and F = k (τ) gel kinetics (F is the degree of conversion of the phosphorylation reaction versus time) [11].



1-60ºC, 2-70ºC, 3-80ºC

Fig. 1. Dependence of F on temperature for the phosphorylation reaction of a polymer based on KO-1 and furfural

In works [10, 11] when analyzing the kinetic regularities of the reaction and diffusion in a polymer granule, it was shown that not the initial stage of the reaction of chemical transformations on polymers with a gel structure (F <0.5), but the limiting reaction of diffusion of a substance into a polymer.

When analyzing the kinetic curves obtained by us (Fig. 1), it can be seen that the kinetic range characteristic of a chemical reaction is observed at F <0.3-0.5 [12].

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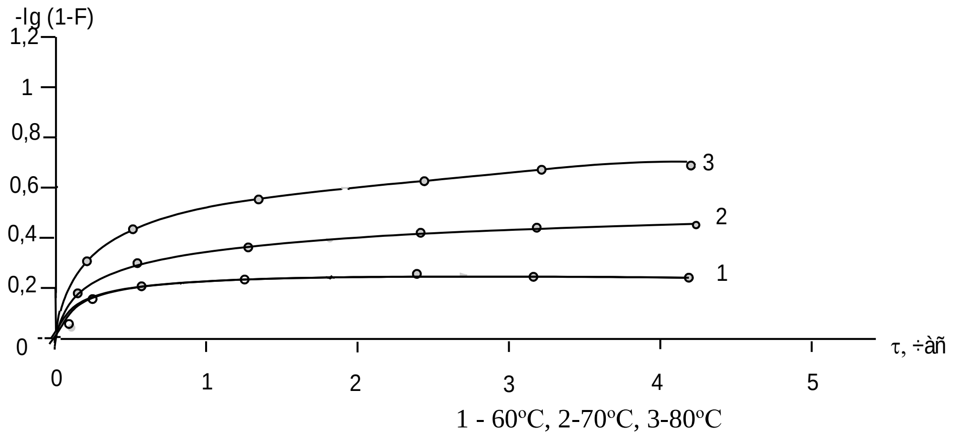


Fig. 2. Dependence of –Ig (1-F) on the phosphorylation reaction of a polymer based on KO-1 and furfural at various temperatures

From the presented kinetic curves (Fig. 2) in coordinates –lg (1-F) –τ for the initial sections were calculated according to the equation –lg (1-F) = k, K– the reaction rate constant and the activation energy of the chemical reaction (Table 1). The activation energy of a chemical reaction was calculated from the tangent of the slope of the straight line from the dependence –lgK versus 1/T (Fig. 3) [13].

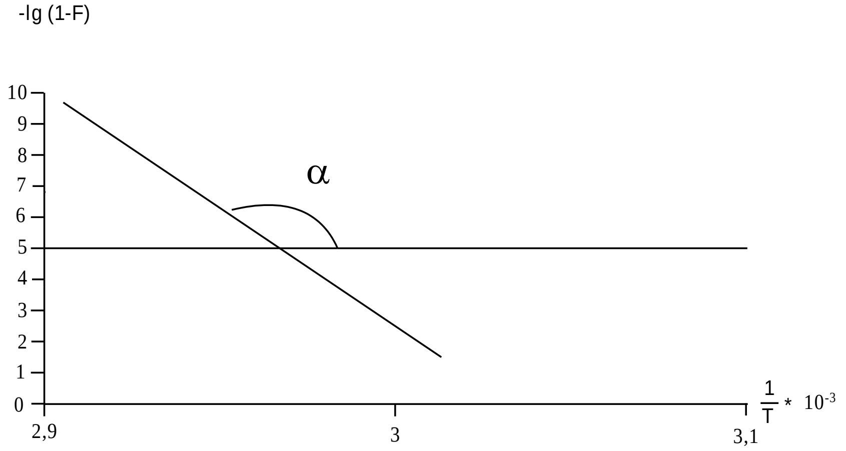


Fig. 3. Dependence of –lgK on 1 / T of the phosphorylation reaction of a polymer based on KO-1 and furfural

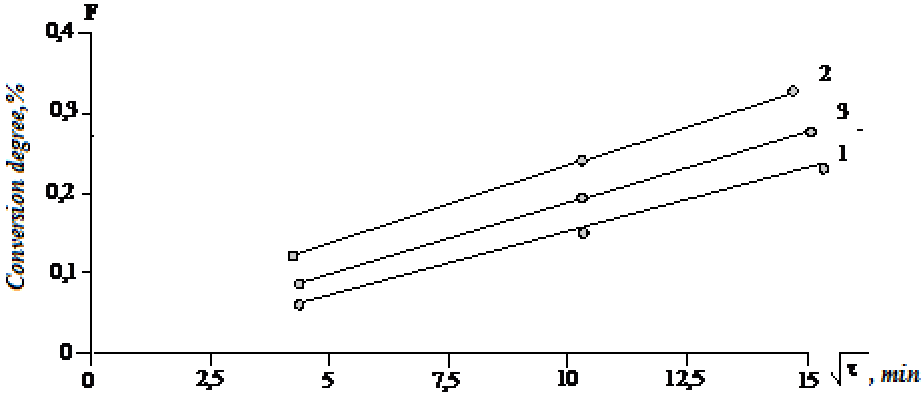
Change in the rate constants of the phosphorylation reaction depending on the temperature in the section F = 0.3-0.5; τ = 60 minutes, consistent with the Arenius equation (Table 1) [12].

Table 1: Values of rate constants and energies of activation and chemical reaction at F = 0.1 - 0.3

T, ºC	Rate constant	–lg K	E, energy of activation kcal/mol.	$\frac{1}{T} \cdot 10^{-3}$
60	0.684	-3.1896	8,86	3,1
70	0.795	-3.1265		3,0
80	0.921	-3.1434		2,7

The limiting effect of gel kinetics was also investigated by the linear dependence in coordinates F = f√τ at F = 0.5> 0.5 (Fig. 4).

The straightness of the dependence of 1o on √τ indicates that at F> 0.5, the effect of gel kinetics increases [14].



T: 1 - 60ºC, 2-70ºC, 3-80ºC

Fig. 4. Dependence of F (degree of conversion) on √τ of the phosphorylation reaction of a polymer based on KO-1 and furfural at different temperatures

Thus, in the initial period (τ = 60 minutes, F≤0.5), the phosphorylation reaction of the synthesized polymer is limited by the chemical reaction stage. Further, as the degree of conversion at F> 0.5 and τ> 60 minutes increases, the effect of the pore diffusion process increases on the rate of the phosphorylation reaction, which is characterized by the penetration of trichlorophosphorusdeep into the thermo polymer, i.e. diffusion into polymer granules becomes the limiting stage of the process. The calculation of the diffusion coefficient at F> 0.5 was carried out according to the method [12].

The experimental data are given in the table.

Table 2: Values of kinetic parameters at different degrees of conversion of the phospholation reaction of a polymer based on furfural and KO-1

ºC	To the reaction rate of a chemical reaction	D 10 cm^2/sec F<0,5	F=0,3-0,5	F-0,5
			$F_{act.chem.reac.}$	$F_{act.dif.}$
			KJ	Mole
60	0,597	0,34	37,12	48,04
70	0,735	0,43		
80	0,869	1,28		

The diffusion activation energy at F> 0.5 was determined from the slope tangent from the –lgD - dependence (Fig. 5) [14].

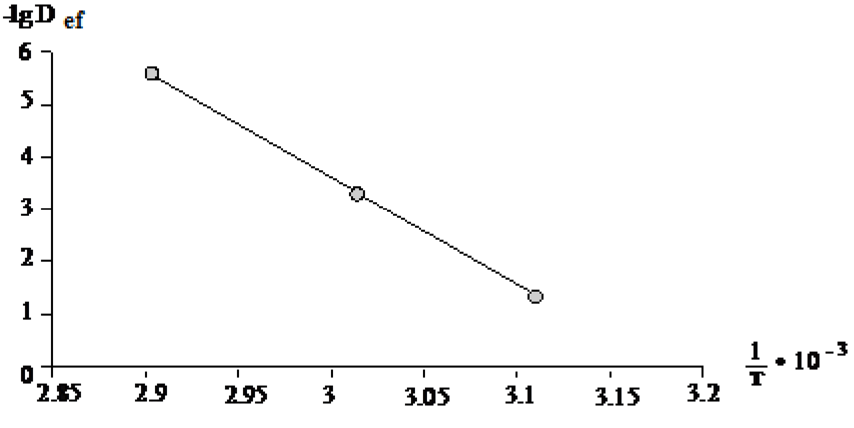


Fig. 5. Dependence of - lgD$_{ef}$ on the phosphorylation reaction of the polymer based on KO-1 and furfural

Based on the experimental data obtained, it can be concluded that the phosphorylation reaction of the polymer based on furfural and KO-1 proceeds with a sufficiently high degree of conversion, the rate of the phosphorylation process is determined at the initial stage by the kinetics of the chemical reaction, and at the final stage by diffusion into the thermo polymer. The results obtained by us coincide with the literature data. To study the reaction of phosphorylation, depending on the duration of the reaction, we used the obtained polymer with a granule diameter (d) equal to 0.25-1.0 mm, swollen in PCl_3 at 25°C at 180%. After reaching the maximum swelling of the polymer in PCl_3, anhydrous $AlCl_3$, used as a catalyst, was introduced into the reaction mixture. Figure 6. shows the dependence of the exchange capacity (SEC) on the duration of the reaction and the phosphorus content in the polymer. The reaction mixture consisted of 4 moles of PCl_3 and 2 moles of $AlCl_3$ per polymer unit. The reaction time at the boiling point of PCl_3 was 8 hours.

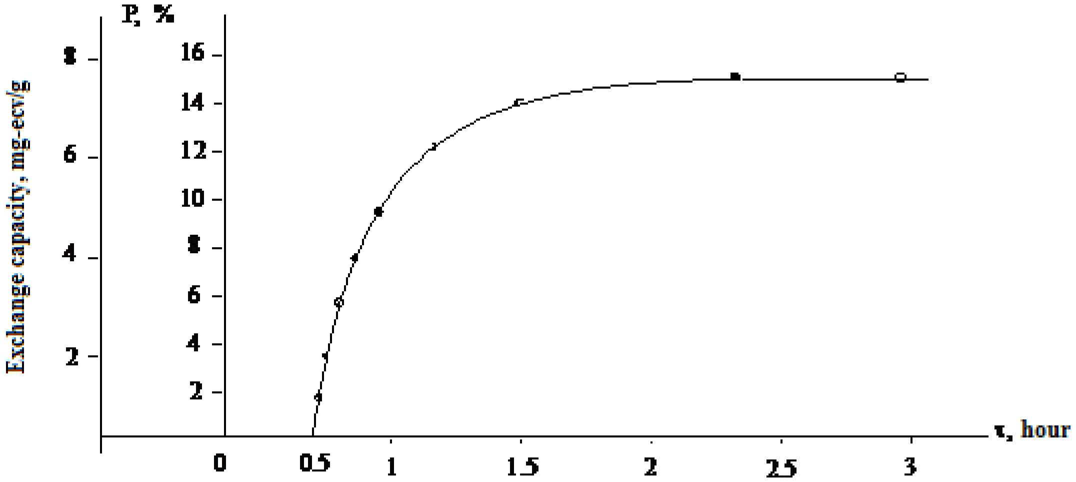


Fig. 6. Dependence of the degree of phosphorylation and exchange capacity on the duration of the phosphorylation reaction

Fig.7 shows the dependence of the degree of phosphorylation on the amount of phosphorus in the polymer and on the concentration of $AlCl_3$ in moles per mole of the obtained unit. It can be seen from Fig. 7 that the maximum number of moles of catalyst $AlCl_3$ corresponds to 2 moles per mole of polymer unit.

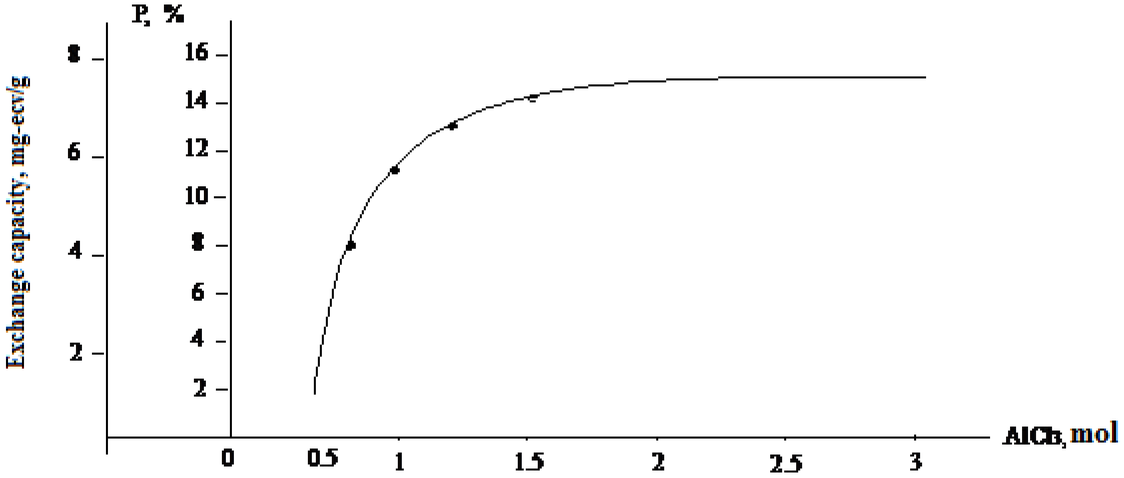


Fig. 7. Dependence of the degree of phosphorylation on the amount of phosphorus in the polymer (P%) and on the concentration of $AlCl_3$ in the reaction mixture, in moles per mole of the polymer unit.

The highest percentage of phosphorus in the resulting polymer - P-16.0%, swelling in PCl3 - 180% is achieved by preliminary holding the polymer in PCl3, taken in a large excess for 1.5-2 hours, introducing two moles of AlCl3 into the mixture for each polymer link and heating the reaction mixture at 70-75 ° C for 8 hours. The intermediate compound was hydrolyzed with distilled water. The polymer retains its original shape and appearance, but acquires the ability to swell in water by 40% in a 0.1N solution of HCl by 40% in a 0.1 N solution of NaOH at 160%, the exchange capacity is 6.5 to 6.0 mEq / g, which corresponds to a phosphorus content of 16% in the polymer. To convert polymeric phosphinous acid into phosphonic acid, the phosphorylated polymer, after its hydrolysis, was oxidized by heating it for 8 hours at 50°C in 25% HNO_3 solution. The surface of the polymer does not change, the maintenance of phosphorus in it also does not change, but the exchange capacity increases to 7.5 mg-eq / g. The swelling capacity of the polymer in water also increases - 130%, in a 0.1N HCl solution - 140%, in a 0.1 N NaOH solution - 190%.

Thus, optimal conditions are adopted for the polymer phosphorylation reaction: the phosphorylation reaction time is τ = 7.0-7.5 hours, the phosphorylation reaction temperature is 70-75 ° C, the weight ratio of KO and furfural is 1.5: 1.0 [3]. The properties of the phosphate cation exchanger obtained under optimal conditions are shown in Table 3.

Table 3: Properties of the obtained phosphate cation exchanger

Main indicators	**Unit of measurement**	**The magnitude of the indicators**
Humidity	%	251
Bulkweight	g/ml	0,68
Specific volume of H-form cation exchanger swollen in water	ml/g	2,8-3,0
Static exchange capacity for 0.1 N solution, mg-eq / g:	meq/g	
NaOH	-	6,5-7,0
NaCl	-	1,2-1,1
$MgCl_2$	-	2,6-2,4
$CaCl_2$	-	2,2-2,3
$CuSO_4$	-	1,3-1,4
$NiSO_4$	-	1,8-1,6
$UO_2(CH_3COO)_2$	mg/g	180-200

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