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KINETIC STUDY OF SORPTION OF 3D-METAL IONS ON SORBENTS MODIFIED WITH POLYVINYL CHLORIDE WITH SOME AMINES

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Annotation
The reaction of polyvinyl chloride with difenilamine was studied in order to modify the complex-forming reaction-active compounds. Their composition and properties were studied. The composition of the obtained product was studied using IR-spectroscopy, scanning electron microscopy, element analysis method.

Keywords
polyvinyl chloride, difenilamine, modification, molecule, sorbent, polymer, membrane, IR-spectroscopy, scanning electron microscop, distilled water, dimethylformamide.

Introduction

The interaction of polyvinyl chloride with dicyclohexylamine, isobutylamine, dipropylamine, ethylenediamine, and tertiary butylamine in tetrahydrofuran has been studied to obtain ion exchange semiconductors. The synthesized polymer amines were purified by precipitation and re-dissolved in tetrahydrofuran. When the solvent finally evaporated, films with ion exchange groups were formed [1].

Ion exchange materials are widely used in various fields of human activity, in in particular, such as pharmaceuticals, petrochemicals and hydrometallurgy, water treatment. One of the important directions is the use of ion exchangers in the

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purification of natural and waste waters from ions of heavy and toxic metals, as well as biologically active substances. One way to get new polymeric materials with the desired physicochemical properties is the modification of existing polymers. In particular, it represents interest in obtaining ion exchangers from polymers widely used in the national economy by modification of materials based on polyvinyl chloride. The modification of polyvinyl chloride was studied in organic media, aqueous solutions, suspensions [2].

Thus, by modifying PVC by methods of polymer-analogous transformations, it is possible to obtain various ion exchangers of both cation-exchange and anion-exchange character. However, to obtain these valuable materials, it is necessary to use granular PVC with a certain particle size. This reaction is complicated due to the influence of diffusion processes on the course of the reaction of chemical transformation in heterogeneous conditions, as well as the presence in the composition of granular PVC of various additives in the form of dioctyl phthalate and destruction stabilizers.

The reactions of chemical transformation of PVC have been studied both in homogeneous and heterogeneous processes in an organic medium, in aqueous solutions, in aqueous suspensions, in a swollen state, in a melt, in solvent-not-solvent systems. In a solution, the nature of the nucleophile is not the only factor influencing the course of the process; in addition, the nature of the solvent, the temperature and duration of the reaction also affect [3].

The main feature of polymer compounds [4-5], is the thermodynamic instability of polymer components, a rule that is generally applicable in practice for most pairs of monomers in different polymer compositions. The lack of thermodynamic stability, of course, leads to the solubility of one monomer in another and, in most cases, that the polymer compounds are a two-phase microheterogeneous system. Depending on the law of distribution, the composition of compounds can form two infinite phases in the whole volume, or one of the components is a dispersed phase-dispersion medium dispersed in a polymer monomer.

There are two approaches to obtaining polymers: the first with a polycondensation mechanism and the second with a polymerization mechanism. Obtaining polemics by polycondensation involves at least three steps takes: copolymer formation by condensation reaction, using functional trialcoxylanes adhesion of alkoxylan monomers to the end groups of the copolemer as a result of hydrolytic condensation formation of sopomer. Technological production of polymers with a polymerization mechanism is somewhat simple because the

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production of the polymer and the introduction of its functional group are in one process combined [6].

Obtaining such sorbents on the basis of polyvinyl chloride planned for production in our country can be very effective. The presence of a highly reactive chlorine atom in PVC allows it to be modified with various reagents and to obtain sorbents with both ion-exchange and chelating properties [7-10].

With the expansion and development of industries, the need for anion-exchange and complex-forming sorbents increases. The synthesis of such sorbents can be achieved by modifying industrial sorbents containing functional groups with various chemical reagents [11].

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Obtaining such sorbents on the basis of polyvinyl chloride planned for production in our country can be very effective. The presence of a highly reactive chlorine atom in PVC allows it to be modified with various reagents and to obtain sorbents with both ion-exchange and chelating properties [15].

Experimental part

Modification of polyvinyl chloride with difenilamine

9.95 g of polyvinyl chloride solution in 82 ml of dimethylformamide was added to a three-mouth flask equipped with a refrigerant and an automatic stirrer and 66.9 g of difenilamine was added dropwise while heating and stirring at 70 ^{o}C. The temperature was then raised to 110–120 ^{o}C, and after stirring for 2–2.5 h at this temperature, a solid, resinous mass was formed. The resulting solid mass was placed in a porcelain bowl and dried in an oven at 60-70 ^{o}C for 4 hours. The dried polymer was pulverized and the low-molecular-weight material was first washed with a 5% solution of KOH in water and then with distilled water until it reacted neutral to the phenolphthalein indicator and air-dried. The resulting sorbent is a gel-like yellow-brown substance. Air-dried sorbent mass 16.96 g, moisture content 12%, reaction yield 88%. The synthesized complex-forming sorbent is partially soluble in water, insoluble and insoluble in organic solvents[16].

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Research results and their discussion

Studying the TGA-DTA-DSK graphs of the complex compound formed as a result of sorption of copper ion to the sorbent synthesized by modifying polyvinyl chloride with diphenylamine, it can be seen that the sample is stable up to 51.2 °C in the temperature range of 20-390 °C. Decomposition occurred at a temperature of 227 °C at a rate of 1.5%/min. The total enthalpy of decomposition is ΔQ = 546.6 J/g – the process is an exothermic effect. At a higher temperature, the sample begins to decompose, and we can see that the total mass reduction is 45.8% compared to the initial sample mass (Figure 1).

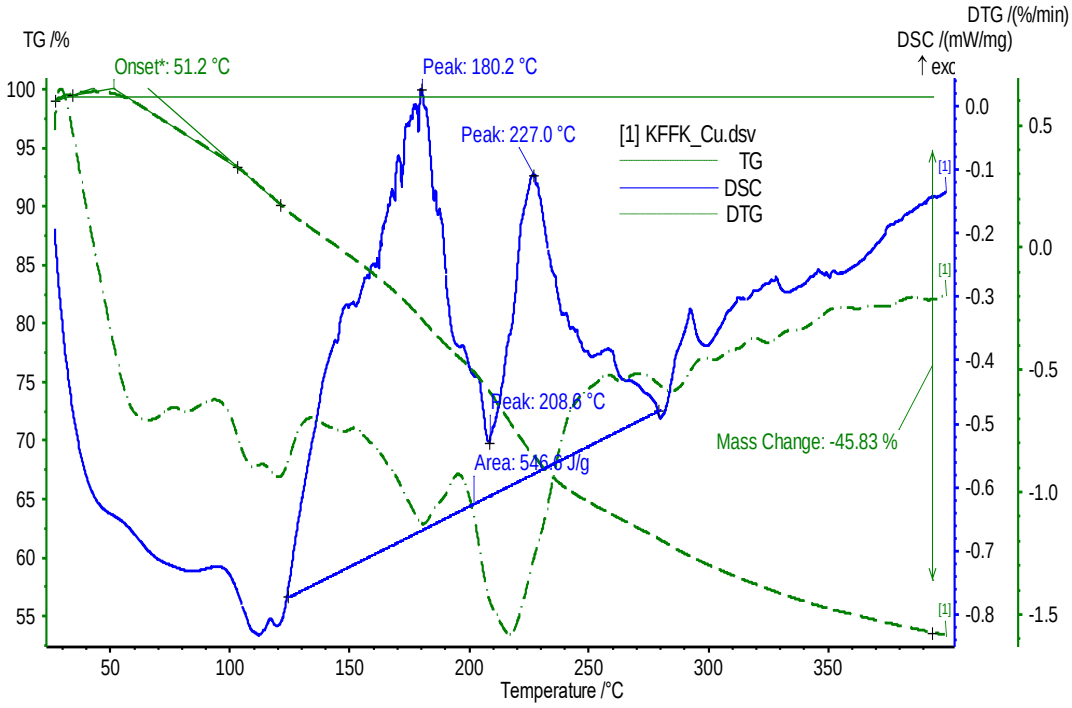

Figure 1. TGA-DTA-DSK graph of the complex compound formed as a result of the sorption of copper (II) ion on a sorbent based on polyvinyl chloride and diphenylamine

Thus, according to the results of differential thermal analysis, the thermal stability of complex compounds formed due to the sorption of metal ions to sorbents increases relatively. In sorbents, thermal decomposition ends at 240-275 °C, while in sorption products it is observed in the temperature range of 340-360 °C.

In order to modify polyvinyl chloride with complex-forming reactive active compounds, the sorbents obtained using diethylamine, monoethanolamine, sodium diethyldithiocarbamate and diphenylamines were subjected to metal ion sorption during the research.

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Chemical modification of polyvinyl chloride with diphenylamine for sorption of Cd (II), Cu (II), Zn (II), Ag (I) ions [17] 1000 g was taken from the obtained sorbent on an analytical balance and placed 4 in 200 ml flasks. Preparation of the solution: 1 eq/g was taken from the metal salts on an analytical balance and transferred to a 1000.0 ml volumetric flask, and distilled water was filled up to the mark of the flask, mixed well, and then the solution was diluted to 4 different 0.0025, 0.005, 0.01, 0.05 Concentrated solutions with N were prepared. 250 ml of each prepared solution was poured and left for 12 hours. Analyzes were carried out with solutions of this concentration at temperatures of 30 °C, 40 °C, 50 °C.

Concentrations of Cd (II), Cu (II), Zn (II), Ag (I) ions in the solution before and after sorption were determined in a spectrophotometer. The sorbed solutions were checked hourly for comparison with the standard solutions, and artificial solutions of each concentration were tested and the average value of the results close to each other was obtained. To determine the concentration of the solutions before and after sorption, the optical densities of the solutions were measured in an ORTIZEN III spectrophotometer and a KFK-2MP concentration photometer. The concentration of absorbed copper ions was determined based on the comparison of the optical densities of the reference and test substances.

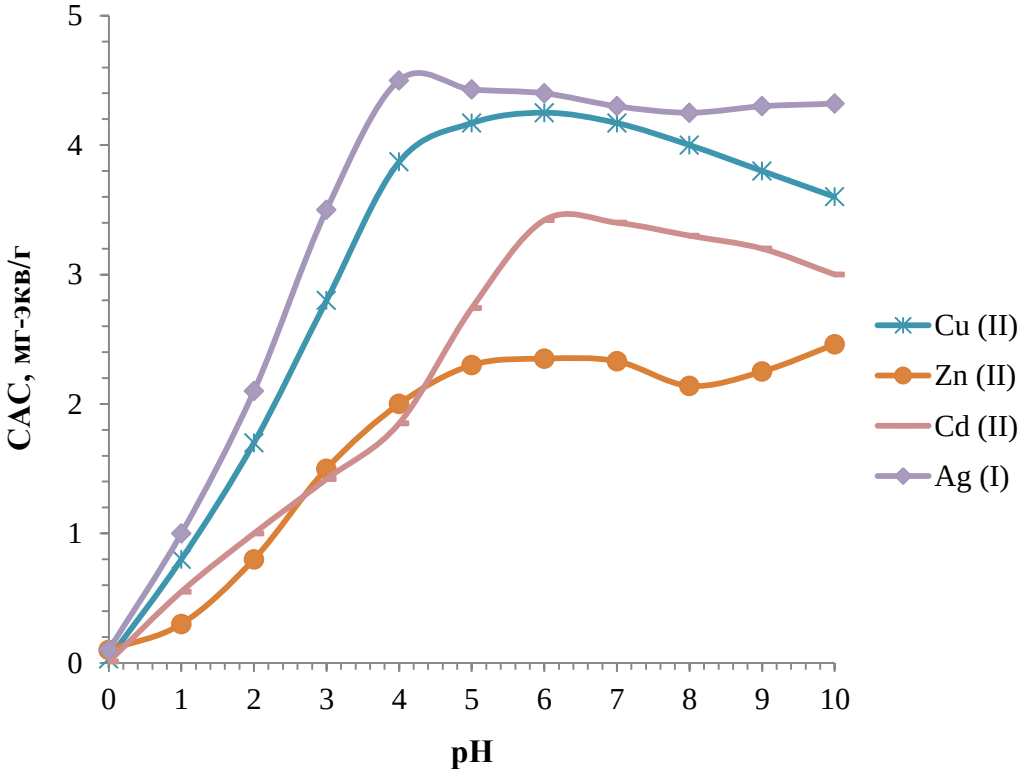

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Figure 1. Dependence of the sorption of some d-metals on the sorbent synthesized by modifying polyvinyl chloride with diphenylamine on the solution medium

The static exchange capacity of the sorbent (mg-equiv/g) depends on the solution environment as follows: Cu (II) – 4.3 (pH=6); Cd (II) – 3.5 (pH=6); Zn (II) - 2.4 (pH=6); Ag (I) – 4.6 (pH=4). It can be seen that in this sorbent, the sorption level of metal ions exceeds the maximum in the range of pH value of solution environment pH=4 to pH=7.

Conclusion

As a result of the studies carried out, a technique for obtaining a sorption material by modifying polyvinyl chloride with diphenylamine has been worked out. The composition of the obtained product was studied using IR-spectroscopy, scanning electron microscopy, element analysis method.

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