FABRICATION OF A WEAKLY BASIC CHEMISORPTION FIBRE WITH ALIPHATIC AMINO GROUPS

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The conditions for fabrication of an anion-exchange fibre with primary and secondary amine groups by preliminary treatment of Nitron fibre with an aqueous solution of hydroxylamine. The effect of the chemical nature of aminating reagents — hydrazine hydrate, ethylenediamine, and triethylenetetramine — on formation of aliphatic amine groups in Nitron fibre was investigated. It was hypothesized that the kinetics of amination is a function of the basicity of the aminating reagent.

The method of polymer-analog transformations is the simplest and most accessible way of fabricating fibres containing chemically active groups. Chemisorption fibres with weakly acid (Vion KN-1) and polyampholytic (Vion KN.AN-3) groups are being manufactured on the pilot-industrial scale with this method. Nitron fibre, which undergoes hydrazidation to form a three-dimensional chemical network, is the starting material [1]. The last stages of the process are defined by the required characteristics of the chemisorbent. In fabrication of Vion KN-1 fibre, the last stage is hydrolysis of nitrile groups, and in fabrication of Vion KN.AN-3 fibre, repeated hydrazidation takes place after hydrolysis.

The presence of itaconic acid in the Nitron fibre, which ensures conducting the hydrazidation reaction at 95°C, is a feature of fabrication of these chemisorption fibres, while hydrazidation is conducted at 120-130°C in a polymer containing no carboxyl groups [2].

As a result of swelling of the polymer in aqueous solutions of hydrazine, the latter reacts with the nitrile groups of the polymer. Vion KN.AN-3 polyampholytic fibre has a static exchange capacity of 1.0-1.5 meq/g for weakly acid groups and 2.0-2.5 meq/g for weakly basic groups. Despite the relatively high concentration of primary and secondary aliphatic amine groups in the polymer, this material has weakly acid groups whose presence not only affects the sorption capacity of the amines but also makes regeneration of the chemisorbent difficult.

For this reason, the conditions of fabricating a chemisorbent with primary and secondary aliphatic amine groups based on Nitron fibre using aqueous solutions of hydrazine, ethylenediamine, and triethylenetetramine as aminating reagents, were elaborated in the present study. Aqueous solutions of hydroxylamine were used as the component for creating a three-dimensional chemical network in the polymer and further reaction of the nitrile groups with the aminating reagents; in reacting with polyacrylonitrile, it forms acrylamidoxime groups according to the reaction:

\[
\begin{align*}
\cdots \text{CH}_2 - \text{CH} \cdots & + \text{NH}_2\text{OH} \rightarrow \\
\text{CN} & = \text{C} - \text{NH}_2 \\
& \| \text{NOH}
\end{align*}
\]

with subsequent formation of glutaraldehydeoxime units:

\[
\begin{align*}
\text{CH}_2 - \text{CH} \cdots & \cdots \text{CH}_2 - \text{CH} \cdots \cdots \text{CH}_2 - \text{CH} \cdots & \cdots \\
\text{C} - \text{NH}_2 & + \text{C} - \text{NH}_2 \rightarrow \\
\text{NOH} & \| \text{NOH} \| \text{NOH} \| \text{NOH}
\end{align*}
\]

Acrylamidoxime and glutaroiimidoxime units, like carboxyl units, ensure the reaction of the amines with polymer nitrile groups at a lower temperature.

Nitron fibre modified with an aqueous solution of hydroxylamine in the concentration of 10 g/liter (Nitron—HA) at a temperature of 80°C was investigated. The degree of conversion of —C=N groups in modification of Nitron fibre was monitored by determining the SEC for weakly basic groups. Then the samples were treated with aqueous solutions of hydrazine hydrate (HH), ethylenediamine (EDA), or triethyltetramine (TETA) in the ratio of 1:50 at the temperature of 90-95°C. The fibres obtained were washed with distilled water and dried to a constant weight at 60°C.

The SEC of the fibre treated with a 30% solution of HH at 95°C for 2 h as a function of the SEC after treatment with hydroxylamine is shown in Fig. 1. The SEC of the fibre increases with an increase in the concentration of amidoxime groups in it. The SEC of the fibre after treatment with a solution of HH remains almost constant and is not a function of the starting capacity after treatment with hydroxylamine (curve 2). For this reason, fibres with a starting SEC of Nitron—HA of 0.3-0.5 meq/g was used for subsequent treatments with the aminating reagents.

The curve of the SEC fibre for anion-exchange groups as a function of the duration of treatment with hydroxylamine is shown in Fig. 2. These data indicate that incorporation of amidoxime and glutaroiimidoxime groups incorporated in Nitron fibre significantly increases the rate of the amination reaction, as observed for fibres containing carboxyl groups [5]. The dependence of the effect of the groups formed after treatment with hydroxylamine on the rate of hydrazidation of nitrile groups suggests that amination of Nitron fibre can also be accelerated with other aminating reagents.