INVESTIGATION OF THE THERMAL PROPERTIES OF THE SYNTHESIZED WEAK-BASE ANION EXCHANGE RESIN

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Annotation. This article presents the results of an investigation into the thermal stability and physicochemical properties of a synthesized weak-base anion-exchange resin based on melamine, diphenylamine, and furfural. A comparative assessment of the thermal and thermohydrolytic stability of the synthesized resin was carried out using the commercially available polycondensation-type anion-exchange resins AN-1 and FAN. The experimental study examined changes in ion-exchange capacity, mass, specific volume, pH of aqueous extracts, and amine group content after thermal treatment in water at 100 °C for 24 and 48 hours. Differential thermal analysis and thermogravimetric analysis were employed to investigate thermal transformations and degradation processes occurring in the polymer structure at elevated temperatures. The experimental results demonstrated that the synthesized anion-exchange resin exhibited higher thermal stability than the AN-1 resin. The incorporation of furfural and diphenylamine into the polymer structure was found to contribute to improved thermal and chemical resistance. The findings are of scientific and practical significance for evaluating the potential application of the synthesized weak-base anion-exchange resin in ion-exchange processes operating under elevated-temperature conditions.

Keywords: weak-base anion-exchange resin, ion-exchange polymer, melamine, diphenylamine, furfural, polycondensation, thermal stability, thermohydrolysis, ion-exchange capacity, differential thermal analysis, thermogravimetric analysis.

Annotatsiya. Mazkur maqolada melamin, difenilamin va furfurol asosida sintez qilingan kuçsiz asosli anionitning termik barqarorligi hamda fizik-kimyoviy xususiyatlari tadqiq etilgan. Sintez qilingan anionitning termik va termogidrolitik barqarorligi sanoatda qöllaniladigan AN-1 va FAN markali polikondensatsion anionitlarning xususiyatlari bilan qiyosiy baholangan. Tadqiqotlar davomida anionitlarning 100 °C haroratdagi suv muhitida 24 va 48 soat davomida termik işlov berilgandan keyingi ion almaşiniş siğimi, massasi, soliştirma hajmi, suvli ekstraktlarining pH qiymati hamda aminoguruhlar miqdoridagi özgarişlar aniqlangan. Şuningdek, differensial-termik va termogravimetrik tahlil usullari yordamida sintez qilingan anionitning yuqori harorat ta'siridagi strukturaviy özgarişlari örganilgan. Tajriba natijalari sintez qilingan anionitning AN-1 anionitiga nisbatan yuqori termik barqarorlikka ega ekanligini körsatgan. Aniqlanişiça, polimer tarkibiga furfurol va difenilaminning kiritilişi uning termik hamda kimyoviy ta'sirlarga çidamliligini oşirişga xizmat qiladi. Olingan natijalar

sintez qilingan anionitdan yuqori harorat şaroitida amalga oşiriladigan ion almaşiniş jarayonlarida foydalaniş imkoniyatlarini baholaşda ilmiy-amaliy ahamiyatga ega.

Kalit sözlar: kuçsiz asosli anionit, ion-almaşinuvçi polimer, melamin, difenilamin, furfurol, polikondensatsiya, termik barqarorlik, termogidroliz, ion almaşiniş siğimi, differensial-termik tahlil, termogravimetrik tahlil.

Аннотация. В статье представлены результаты исследования термической устойчивости и физико-химических характеристик синтезированного слабоосновного анионита на основе меламина, дифениламина и фурфурола. Проведена сравнительная оценка термической и термогидролитической устойчивости полученного анионита с промышленными поликонденсационными анионитами АН-1 и ФАН. В ходе экспериментальных исследований изучены изменения обменной ёмкости, массы, удельного объёма, водородного показателя водных вытяжек и содержания аминогрупп после термической обработки анионитов в водной среде при температуре 100°C в течение 24 и 48 часов. С использованием методов дифференциально-термического и термогравиметрического анализа исследованы процессы термических превращений и деструкции полимерной структуры при повышенных температурах. Установлено, что синтезированный анионит характеризуется более высокой термической устойчивостью по сравнению с анионитом АН-1. Показано, что введение фурфурола и дифениламина в структуру полимерного анионита способствует повышению его термической и химической стойкости. Полученные результаты имеют научное и практическое значение для оценки возможности применения синтезированного анионита в ионообменных процессах, протекающих при повышенных температурах.

Ключевые слова: слабоосновный анионит, ионообменный полимер, меламин, дифениламин, фурфурол, поликонденсация, термическая устойчивость, термогидролиз, обменная ёмкость, дифференциально-термический анализ, термогравиметрический анализ.

Introduction

The thermal stability of ion-exchange polymers is an important factor determining their efficiency, durability, and applicability in various industrial processes. Anion-exchange resins are widely used in water purification, wastewater treatment, hydrometallurgy, chemical separation, and the recovery of valuable components from industrial solutions. However, their practical application at elevated temperatures is often limited by the thermal degradation of functional groups and changes in the physicochemical properties of the polymer matrix [1].

The thermal resistance of anion-exchange resins depends on several factors, including the chemical composition of the polymer backbone, the nature of ionogenic functional groups, the degree of crosslinking, the ionic form of the resin, and the surrounding medium. The presence of primary, secondary, and tertiary amino groups determines the basic properties of weak-base anion exchangers, while the chemical structure and accessibility of these groups influence their ion-exchange performance [2].

Literature review

Tulupov and Polyanskii [3] conducted a comprehensive investigation of the thermal stability of anion-exchange resins in different media, including air, water, aqueous solutions, and organic solvents. The authors demonstrated that thermal treatment may result in a decrease in exchange capacity due to deamination, degradation of functional groups, and structural transformations within the polymer matrix. Particular attention was paid to the mechanisms and kinetics of ion-exchange resin degradation. Their findings established an important theoretical basis for evaluating the thermal resistance of anion-exchange materials.

Ezzeldin et al. [4] investigated the synthesis and thermal properties of anion exchangers derived from vinylbenzyl chloride–divinylbenzene copolymers. Thermogravimetric analysis revealed several characteristic stages of thermal decomposition. The initial stage was associated primarily with the removal of moisture and residual solvents, while subsequent stages involved the decomposition of functional groups and degradation of the polymer backbone. The authors found that the chemical composition and ionic form of the synthesized resins significantly influenced their thermal stability. The onset temperature of degradation for the synthesized resin in the hydroxide form was approximately 165°C, compared with 149°C for a commercial reference resin.

The development of polycondensation-type anion exchangers represents another promising approach to improving the physicochemical characteristics of ion-exchange polymers. Yuldashev et al. [5] investigated the polycondensation of melamine with furfural and established the influence of reaction temperature, reagent ratio, and synthesis conditions on the resulting polymer properties. The authors reported that increasing the polycondensation temperature from 100 to 120°C improved the exchange capacity of the synthesized material from approximately 4.0 to 4.8–5.0 meq/g. The optimum reaction temperature was identified as 120°C, at which the polymer exhibited favorable physicochemical and mechanical properties.

Methodology

The incorporation of nitrogen-containing heterocyclic compounds and aromatic fragments into polycondensation networks is of particular interest in designing thermally resistant ion-exchange materials. Melamine contains a nitrogen-rich triazine ring, while diphenylamine introduces aromatic structural fragments. Furfural serves as a reactive component in the formation of the polymer network. Such structural features may contribute to increased network rigidity and resistance to thermally induced structural changes. Nevertheless, the actual improvement in thermal stability depends on the resulting chemical bonds, crosslink density, and degradation mechanisms and must be confirmed experimentally.

Recent studies have further demonstrated that the thermal behavior of anion exchangers is strongly influenced by their chemical composition and operating environment. Kociołek-Balawejder and Mucha [6] investigated the effect of copper sulfide particles on the thermal decomposition of anion-exchange polymers. Their results showed that the presence of inorganic components can substantially modify the

decomposition pathway and reduce the temperature required for polymer backbone degradation. The study also emphasized the importance of distinguishing thermal processes occurring in oxidative and inert atmospheres.

The thermal degradation of ion-exchange materials generally involves several overlapping physicochemical processes. At relatively low temperatures, mass loss is frequently associated with the removal of physically adsorbed moisture and other volatile components. At higher temperatures, decomposition of chemically less stable fragments and functional groups may occur. Further heating may result in extensive degradation of the polymer backbone, accompanied by the release of gaseous products and the formation or oxidation of solid residues.

Thermogravimetric analysis (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) are among the most widely used techniques for investigating these transformations. TG enables the determination of mass changes as a function of temperature, DTG identifies temperature intervals characterized by maximum rates of mass loss, and DTA provides information about thermal effects accompanying physical and chemical transformations.

Vyazovkin et al. [7], in their recommendations developed for the International Confederation for Thermal Analysis and Calorimetry (ICTAC), emphasized the importance of correctly interpreting multistep thermal decomposition processes. The authors demonstrated that overlapping thermal events may complicate the determination of kinetic parameters and proposed methodological approaches for evaluating individual degradation stages. These recommendations are particularly relevant to crosslinked ion-exchange polymers, whose decomposition may involve simultaneous dehydration, functional-group degradation, and polymer-network breakdown.

Recent investigations of weak-base anion exchangers have also confirmed the multistage character of thermal degradation. Adinaeva et al. [8] studied the non-isothermal decomposition of a weak-base anion exchanger containing amidine groups, based on an acrylonitrile–divinylbenzene copolymer. Two principal temperature regions were identified: 26.39–278.63°C, associated with dehydration and the degradation of relatively labile structural fragments, and 278.63–600.89°C, corresponding to the decomposition of functional groups and the polymer backbone. The reported activation energies for these regions were approximately 55 and 180 kJ/mol, respectively.

Despite these investigations, the available literature indicates that the thermal properties of anion-exchange polymers are highly dependent on their individual chemical structures. Consequently, the results obtained for conventional styrene–divinylbenzene and acrylic ion-exchange resins cannot be directly transferred to polycondensation-type materials based on melamine, furfural, and aromatic amines.

Furthermore, thermal stability evaluated by heating a dry polymer in air is not equivalent to hydrothermal stability under aqueous operating conditions. Anion-exchange functional groups may undergo hydrolysis or other chemical transformations in water even at temperatures substantially below the onset of intensive polymer-backbone decomposition. Therefore, the preservation of exchange capacity, changes in swelling behavior, mass loss, and the release of amine-containing compounds into the

aqueous phase must be considered when assessing the practical thermal resistance of anion exchangers.

Particular attention should be paid to evaluating the relationship between polymer composition, thermal degradation stages, and changes in ion-exchange properties under hydrothermal conditions.

Analysis and results

Accordingly, the objective of the present study is to investigate the thermal and hydrothermal stability of a synthesized weak-base anion-exchange polymer based on melamine, diphenylamine, and furfural, to identify the principal stages of its thermal decomposition using TG, DTG, and DTA methods, and to compare its stability with that of conventional polycondensation-type anion exchangers AN-1 and FAN.

The thermal stability of the investigated anion-exchange resins was evaluated in water at 100°C and in air using differential thermal analysis (DTA). The anion-exchange resins were prepared for testing according to the established experimental procedure.

Table 1

Analysis of aqueous extracts of anion-exchange resins after thermal treatment

Anion-exchange resin	pH after 24 h	Amine group content after 24 h (meq/g)	Weight loss after 24 h (%)	pH after 48 h	Amine group content after 48 h (meq/g)	Weight loss after 48 h (%)
Synthesized anion exchanger	7.20	0.0	–	7.35	0.2	2.85
AN-1	8.95	1.2	4.5	9.50	1.6	7.0

The anion-exchange resins were tested in their hydroxide (OH^-) form. Their thermal stability was characterized by changes in exchange capacity, weight, and specific volume.

Thermal stability in water, i.e., resistance to thermohydrolysis, was investigated under controlled experimental conditions. Weighed samples of the anion-exchange resins were placed in glass ampoules, filled with distilled water, hermetically sealed, and maintained at the boiling temperature of water for 24 and 48 hours.

Following thermal treatment, the ampoules were opened, and the anion-exchange resins were separated from the aqueous extracts. The samples were subsequently dried to an air-dry state, weighed, and analyzed to determine their exchange capacity and specific volume (Table 1).

The results presented in Table 1 indicate that the properties of the investigated anion-exchange resins undergo changes at the boiling temperature of water, with the extent of these changes increasing as the duration of thermal treatment increases.

The decrease in the exchange capacity of the anion-exchange resins following thermal treatment suggests the cleavage of amine groups (deamination) or structural

rearrangements that apparently result in the conversion of ionogenic functional groups into an inactive state. This assumption is supported by the reduction in the specific volume of the anion-exchange resins after thermal treatment.

When anion-exchange resins are heated in water, the decrease in their exchange capacity is associated with thermal deamination, which involves hydrolytic reactions resulting in the release of amine-containing groups into the aqueous phase.

Therefore, the resistance of the anion-exchange resins to thermohydrolysis was additionally evaluated by monitoring changes in the pH of their aqueous extracts. For this purpose, the aqueous extracts obtained after thermal treatment were combined with the washing solutions, and their pH values and amine group contents were determined according to the established analytical procedure. The experimental results are presented in Table 2.

According to the experimental observations, after 48 hours of thermal treatment, the exchange capacity of the synthesized anion-exchange resin decreased from 5.6 to 5.2 meq/g. This change was associated with the presence of amine groups in the aqueous extract at a concentration of 0.6 meq/g (pH = 7.25) [9].

In contrast, the exchange capacity of the AN-1 anion-exchange resin decreased from 6.4 to 3.1 meq/g after 48 hours of thermal treatment, while the aqueous extracts contained 1.6 meq/g of amine groups (pH = 9.5).

These findings indicate that the synthesized anion-exchange resin exhibits considerably higher thermal stability than the conventional AN-1 anion-exchange resin.

Table 2

Thermal stability of anion-exchange resins in water at 100°C

Anion exchange resins	Before thermal treatment			After thermal treatment					
				24 h			48 h		
	Static exchange capacity, determined using a 0.1 N HCl solution	Bulk density in g/ml	Specific volume units are reproduced from the source, mg/l	Static exchange capacity, determined using a 0.1 N HCl solution	Bulk density in g/ml	Specific volume units are reproduced from the source, mg/l	Static exchange capacity, determined using a 0.1 N HCl solution	Bulk density in g/ml	Specific volume units are reproduced from the source, mg/l
	5.51	5.2	3.0	5.4	5.2	2.8	5.3	0.52	2.65
FAN	4.5	0.45	4.0	4.3	0.5	3.2	4.1	0.5	2.9
AN -1	6.4	0.5	3.2	4.78	0.5	2.5	4.1	0.5	2.3

The thermal stability of the anion-exchange resins in air was investigated by differential thermal analysis using a derivatograph. The corresponding thermal analysis curves are presented in Figures 1 and 2 [10].

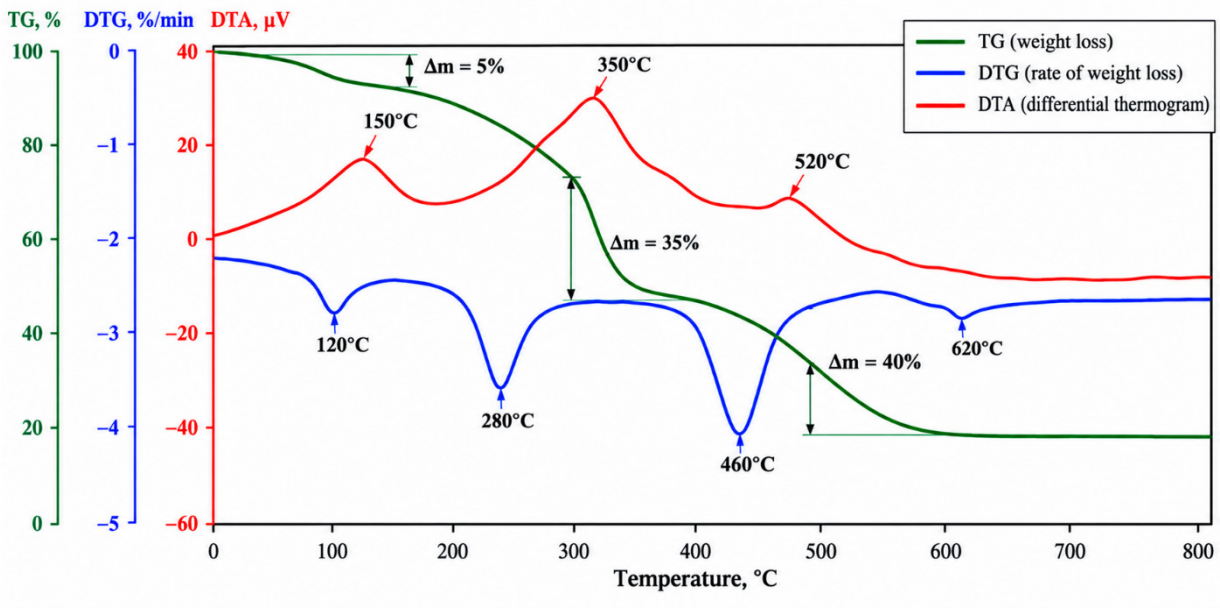
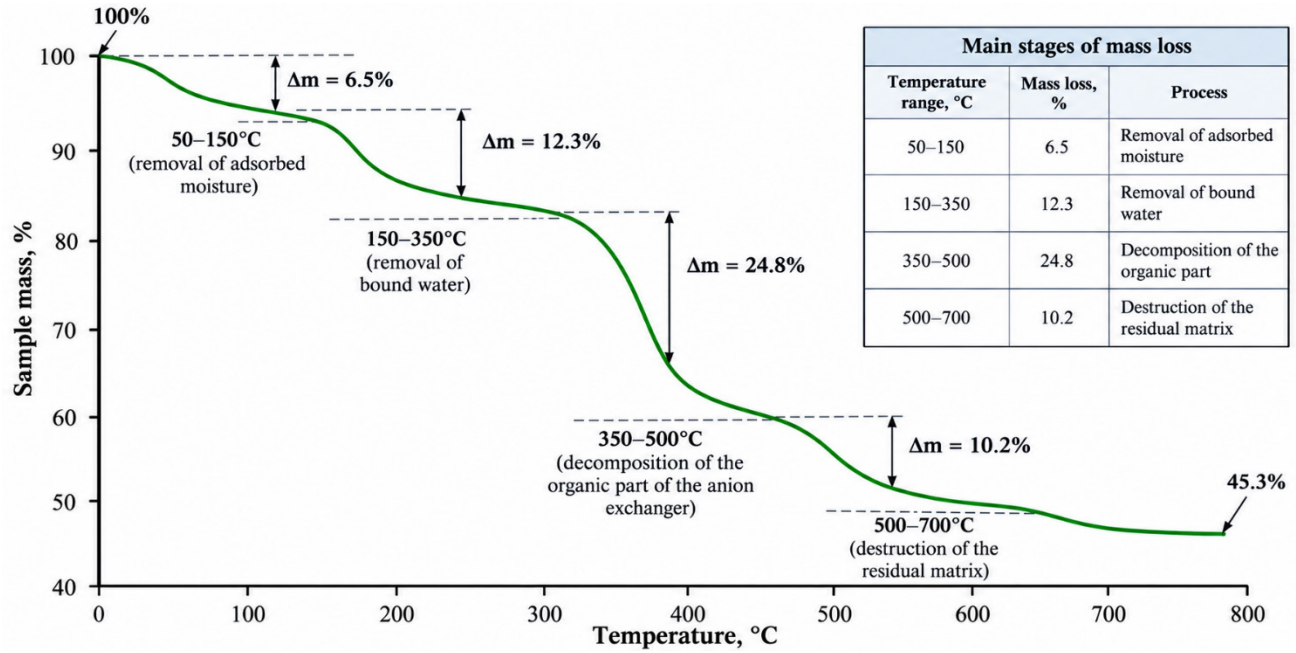


***Fig. 1**. Differential thermal analysis (DTA) curve*

The thermogram of the investigated anion-exchange resin exhibits two distinct thermal effects: the first in the temperature range of 100–200°C and the second in the range of 280–450°C. The first endothermic effect can be attributed to the dehydration of the anion-exchange resin [11].



Main stages of mass loss		
Temperature range, °C	Mass loss, %	Process
50–150	6.5	Removal of adsorbed moisture
150–350	12.3	Removal of bound water
350–500	24.8	Decomposition of the organic part
500–700	10.2	Destruction of the residual matrix

***Fig. 2**. Thermogravimetric curve (weight-loss curve)*

The cleavage of functional groups in the polymeric anion-exchange resin begins at approximately 280°C. The polymer framework demonstrates a high degree of resistance to thermal degradation.

When the anion-exchange resin is heated to 800°C for 50 minutes, the weight loss reaches approximately 40–50%, while the external appearance of the polymer remains unchanged [12].

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