ANNOTATION

to the dissertation work of Arshyn Zhengis on the topic "Preparation of a Novel Multifunctional Zwitterionic Polymeric Membrane", submitted for the degree of Doctor of Philosophy (PhD) in the educational program "8D05301-Chemistry"

The dissertation work is presented in the form of a *series of articles* published by the doctoral student in accordance with the requirements of the rules for awarding academic degrees, approved by the order of the minister of Science and Higher Education of the Republic of Kazakhstan №7 dated 09.01.2023.

The relevance of research.

Among various classes of functional polymers, zwitterionic polymers stand out for their unique molecular structure that incorporates both cationic and anionic groups while maintaining an overall neutral charge.

In recent years, researchers have focused on developing alternative zwitterionic materials with improved performance and simpler synthesis routes. Among such zwitterionic materials, sulfobetaine (SB)-based polymers have emerged as promising candidates due to their biomimetic properties, excellent biocompatibility, non-cytotoxicity, chemical stability, and ease of preparation. Typical representatives, such as sulfobetaine methacrylate (SBMA), poly(sulfobetaine methacrylamide) (pSBMAm), poly(sulfobetaine-1-vinylimidazole) (pSB1VI), poly(sulfobetaine-2-vinylpyridine) (pSB2VP), and poly(sulfobetaine-4-vinylpyridine) (pSB4VP), can be synthesized through the nucleophilic ring-opening reaction of 1,3-propane sultone with various tertiary amines.

Recent studies demonstrate that zwitterionic polymers exhibit pH-independent charge neutrality and high hydrophilicity, making them highly suitable for membrane-based water purification technologies. Their strong hydration layer and resistance to nonspecific adsorption make them especially attractive for applications in desalination, ion separation, and antifouling membrane development. Thus, research into sulfobetaine-based zwitterionic polymers is of great scientific and practical relevance for addressing global challenges related to clean water production and sustainable environmental technologies.

Research goal. The primary goal of this research is to investigate the fundamental aspects of the synthesis and characterization of zwitterionic monomers and polymers, focusing on the modification of linear, vinyl, and aromatic heterocyclic functional groups through reactions with 1,3-propanesultone. This synthetic strategy enables the development of advanced zwitterionic materials with controlled structural and physicochemical properties suitable for membrane-based separation technologies.

Furthermore, the research aims to develop, understand, and apply zwitterionic polymers, particularly SBMA, for the design of high-performance, antifouling, and selective membranes for water treatment applications. By systematically exploring all stages from molecular synthesis and structural optimization, including the incorporation of functional materials, to membrane fabrication and performance evaluation, this study seeks to establish a comprehensive understanding of the structure–property–function relationships that govern the behavior of zwitterionic materials in aqueous environments.

Achieving this goal involves solving the following tasks:

1. To conduct a comprehensive literature review on the use of zwitterionic polymers for membrane-based water treatment, with emphasis on their antifouling behavior, hydration mechanisms, ion selectivity, and applicability in nanofiltration membranes.
2. To synthesize four zwitterionic monomers and polymers: poly(sulfobetaine methacrylamide) (pSBMAm), poly(sulfobetaine-1-vinylimidazole) (pSB1VI), poly(sulfobetaine-2-vinylpyridine) (pSB2VP), and poly(sulfobetaine-4-vinylpyridine) (pSB4VP).

3. To characterize the synthesized polymers in terms of their thermal behavior and self-assembly properties.

4. To develop a hierarchically engineered nanocomposite membrane based on SBMA by integrating zeolitic imidazolate framework-8 (ZIF-8) and SBMA into a polyacrylonitrile–polyvinylpyrrolidone (PAN–PVP) matrix, and to evaluate its structural, physicochemical, and separation performance in membrane purification technology.

Research object. Zwitterionic monomers, functionalized monomers and their corresponding polymers, as well as hybrid composite materials based on zwitterionic polymers with ZIF-8 and incorporated into a polyacrylonitrile–polyvinylpyrrolidone (PAN–PVP) matrix.

Research methods. The study employed nucleophilic ring-opening reactions and redox-induced polymerization for the synthesis of zwitterionic monomers and polymers, followed by characterization of their structural and physicochemical properties.

Comprehensive material analysis was carried out using advanced characterization techniques, including nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Elemental mapping, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), zeta potential measurements, Organic Elemental Analysis (CHNS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Additionally, density functional theory (DFT) and molecular dynamics (MD) calculations were used to study molecular-level interactions and support the interpretation of experimental results.

Research hypothesis:

1. The successful synthesis of four zwitterionic polymers - poly(sulfobetaine methacrylamide) (pSBMAm), poly(sulfobetaine-1-vinylimidazole) (pSB1VI), poly(sulfobetaine-2-vinylpyridine) (pSB2VP), and poly(sulfobetaine-4-vinylpyridine) (pSB4VP) is achievable using appropriate polymerization strategies.

2. The chemical structure of the synthesized zwitterionic polymers significantly influences their thermal behavior and self-assembly properties, leading to distinct thermal stability and self-organized morphologies among pSBMAm, pSB1VI, pSB2VP, and pSB4VP.

3. Integrating ZIF-8 into a SBMA based polymer matrix will create a synergistic zwitterion–metal–organic framework (MOF) interface that significantly enhances membrane performance. The hierarchical SBMA–ZIF-8 hybrid structure is expected to yield superior ion and dye rejection, higher permeability, and improved antifouling behavior relative to membranes containing only SBMA or only ZIF-8, due to the combined contributions of MOF porosity and zwitterionic hydration.

The main rules of the dissertation submitted for defense:

1. Zwitterionic monomers were first synthesized via nucleophilic ring-opening of 1,3-propanesultone, enabling efficient incorporation of sulfobetaine groups. These monomers were subsequently polymerized to yield four zwitterionic polymers (pSBMAm, pSB2VP, pSB3VP, and pSB4VP). Despite identical functionalization chemistry, the polymers exhibited markedly different molecular weights, ranging from 35,810 Da (pSB2VP) to 197,241 Da (pSBMAm), underscoring the decisive role of backbone structure in polymer growth.

2. The zwitterionic polymers exhibited distinct thermal properties, with glass transition temperatures increasing from 276.52 °C for pSBMAm to 313.69 °C for pSB4VP, indicating progressively restricted chain mobility. pH-dependent TEM analysis revealed pronounced differences in self-assembly behavior: pSBMAm formed the largest and most complex fractal or dendritic nanostructures, whereas pSB2VP assembled into smaller, less branched morphologies.

3. The SBMA–ZIF-8 hybrid membrane achieved a pure water flux of 71.96 $L \cdot m^{-2} \cdot h^{-1}$ an demonstrated high rejection efficiency for Cd^{2+} (95.6%), Cu^{2+} (93.3%), Pb^{2+} (97.8%), methyl orange (98.9%), and methylene blue (98.4%), while maintaining ~93% performance stability over ten consecutive filtration cycles.

Scientific results:

1. A comparative structure–property–self-assembly relationship was established for a series of sulfobetaine polymers synthesized via nucleophilic ring-opening of 1,3-propanesultone. It was discovered that the chemical nature of the functional groups (linear, vinyl, and aromatic heterocyclic) fundamentally governs the thermal transitions, molecular weight distributions, and nanostructured self-assembly of the resulting polymers. The pSBMAm polymer demonstrated the highest molecular weight and formed the most extended fractal/dendritic structures at alkaline pH, while pSB4VP exhibited the greatest thermal stability, revealing a direct correlation between monomer structure, polymerization behavior, and nanoscale morphology.

2. A comprehensive scientific framework was developed that, for the first time, systematically unifies the antifouling mechanisms, hydration behavior, and membrane performance trends of SBMA-based membrane systems. The analysis revealed that SBMA's intrinsic electroneutrality, strong zwitterionic hydration layer, and steric repulsion collectively dictate its antifouling effectiveness across various integration strategies, including surface coating, surface grafting, and physical blending. The review identified the principal chemical and morphological parameters that control flux recovery, fouling resistance, and ion selectivity, thereby defining the key structure–property–performance relationships necessary for designing next-generation SBMA nanofiltration membranes.

3. A new class of hierarchically engineered SBMA–ZIF-8 hybrid membranes was developed, demonstrating the synergistic functional interface between the zwitterionic polymer matrix and the porous metal–organic framework. This hybrid interface significantly enhanced water transport and selective rejection mechanisms by combining the hydration-limited exclusion of SBMA with the molecular sieving characteristics of ZIF-8. The resulting membrane achieved a high pure water flux of 71.96 $L \cdot m^{-2} \cdot h^{-1}$ and exceptional rejection of heavy-metal ions and dyes, while maintaining approximately 93% of its performance over repeated filtration cycles, revealing the critical role of polymer–MOF interactions in enabling durable and high-efficiency separation processes.

Novelty and importance of obtained results:

The first article (review), "Zwitterionic SBMA-Based Nanofiltration Membranes: Synthesis Techniques, Antifouling Mechanisms, and Future Perspectives," presents a systematic evaluation of the chemistry, morphology, and integration strategies of SBMA in membrane technologies. By consolidating antifouling mechanisms, hydration-layer behavior, and membrane performance across coating, grafting, and blending methods, this review clarifies the structure–property–performance relationships that govern SBMA membranes. The insights gained are important for guiding the rational design of next-generation nanofiltration materials with enhanced flux recovery, fouling resistance, and ion selectivity—critical features for modern water treatment and desalination systems.

The second article (research), "Preparation of Zwitterionic Sulfobetaines and Study of Their Thermal Properties and Nanostructured Self-Assembling Features," introduces a comprehensive approach for synthesizing and characterizing sulfobetaine-based polymers with diverse functional architectures. The work demonstrates how modifying linear, vinyl, and aromatic heterocyclic groups enables precise control over thermal transitions, molecular weights, and pH-responsive self-assembly. This provides important new opportunities for designing zwitterionic polymers with tunable nanoscale organization, which is highly relevant for applications in membrane engineering, colloidal stabilization, and advanced soft-matter systems.

The third article (research), “Zwitterion–MOF Functional Interface Enabling Robust Ion and Dye Rejection in Water Filtration,” reports the development of a hierarchically engineered SBMA–ZIF-8 hybrid membrane that achieves significantly improved filtration performance through synergistic polymer–MOF interactions. The hybrid architecture enhances water transport, stabilizes zwitterionic hydration layers, and introduces efficient molecular sieving pathways, resulting in excellent rejection of heavy-metal ions and dyes along with high flux and operational durability. This innovation is highly impactful for advancing high-performance membrane technologies capable of addressing global challenges in clean water production and wastewater remediation.

Theoretical and practical importance of the work.

The research provides important theoretical contributions by revealing how variations in zwitterionic monomer structures, including linear, vinyl, and aromatic heterocyclic types, govern the thermal stability, molecular weight distribution, and self-assembly behavior of sulfobetaine polymers. The work also systematizes the fundamental mechanisms underlying fouling resistance, hydration-layer formation, and ion selectivity in zwitterionic membrane systems, establishing clear structure–property–performance relationships. In addition, the study demonstrates how zwitterionic functional groups enhance water transport and selective rejection processes in membrane materials, thereby deepening scientific understanding of polymer hydration, charge neutrality, and separation behavior.

From a practical perspective, the findings offer a foundation for the development of more efficient and durable membrane materials for water treatment. The demonstrated antifouling behavior, strong hydration effects, and stable separation performance of zwitterionic polymers provide pathways for improving flux recovery, reducing fouling, and increasing rejection efficiency in nanofiltration and ultrafiltration processes. These results have the practical importance in supporting the creation of next-generation membrane systems capable of addressing major challenges in desalination, wastewater purification, and industrial water reuse.

Connection of the work with the plan of state scientific programs. This research received financial support from Project AP13067633, “Theoretical and Experimental Studies of Amphiphilic Polybetaine Self-Assembly and Function (2022-2024),” funded by the Ministry of Science and Higher Education.

Publications and author's personal contribution to the research. Three scientific papers were published based on the results of this dissertation, including two research articles and one review article. In addition, one article was published in a journal recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Higher Education and Science. The first article, a review titled “Zwitterionic SBMA-based Nanofiltration Membranes: Synthesis Techniques, Antifouling Mechanisms, and Future Perspectives,” appeared in Polymer (Q2, 82% percentile, CiteScore 7.7). The second article, research titled “Preparation of Zwitterionic Sulfobetaines and Study of Their Thermal Properties and Nanostructured Self-Assembling Features,” was published in Nanomaterials (Q2, 85% percentile, CiteScore 9.2). The third article, “Zwitterion–MOF Functional Interface Enabling Robust Ion and Dye Rejection in Water Filtration,” was published in ACS Applied Materials & Interfaces (Q1, 91% percentile, CiteScore 14.5).

1. **Zhengis, A.;** Yergesheva, A.; Amrenova, Y.; Abutalip, M.; Nuraje, N. Zwitterionic SBMA Based Nanofiltration Membranes: Synthesis Techniques, Antifouling Mechanisms, and Future Perspectives. Polymer (Guildf) 2025, 337, No. 128944, https://doi.org/10.1016/j.polymer.2025.128944, is a review article in which Arshyn Zhengis is the first author. Her contributions include conceptualization, formal analysis, data curation, writing of the original draft, and writing and editing of the final manuscript.

2. Amrenova, Y.; **Zhengis, A.**; Yergesheva, A.; Abutalip, M.; Nuraje, N. Preparation of Zwitterionic Sulfobetaines and Study of Their Thermal Properties and Nanostructured Self Assembling Features. Nanomaterials 2025, 15 (1), 58, https://doi.org/10.3390/nano15010058, presents the synthesis and characterization of sulfobetaine monomers. In this work, Arshyn Zhengis is a co-author and contributed to data curation, investigation, methodology, validation, visualization, and drafting the original version of the manuscript.

3. **Zhengis, A**.; Ospanova, A.; Amrenova, Y.; Askar, P.; Aldongarov, A.; Karibayev, M.; Aliyev A.; Abutalip, M.; Nuraje, N. Zwitterion–MOF Functional Interface Enabling Robust Ion and Dye Rejection in Water Filtration. ACS Appl Mater Interfaces 2025, https://doi.org/10.1021/acsami.5c16282, highlights the development of a zwitterion–MOF hybrid membrane system. In this work, Arshyn Zhengis is the first author and was responsible for methodology, investigation, and writing the original draft of the manuscript.

4. **Zhengis A**, Amrenova Y, Yergesheva A, Kanzhigitova D, Imekova G, Toktarbay Z, Toktarbaiuly O, Abutalip M, Nuraje N (2024) Structural Studies and Applications of Sulfobetaine-Based Polybetaines at Interfaces. EURASIAN JOURNAL OF CHEMISTRY. https://doi.org/10.31489/2959-0663/1-24-3, this work reports the development of a zwitterion–metal–organic framework hybrid membrane system. Arshyn Zhengis served as the first author and led the methodology, experimental investigation, and preparation of the original manuscript.