



## Research Paper

# Pervaporation multilayer membranes based on a polyelectrolyte complex of $\lambda$ -carrageenan and chitosan



Svetlana V. Kononova<sup>a</sup>, Aleksandra V. Volod'ko<sup>b</sup>, Valentina A. Petrova<sup>a</sup>, Elena V. Kruchinina<sup>a</sup>, Yulia G. Baklagina<sup>a</sup>, Evgeniy A. Chusovitin<sup>c</sup>, Yury A. Skorik<sup>a,d,e,\*</sup>

<sup>a</sup> Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr. VO 31, St. Petersburg 199004, Russian Federation

<sup>b</sup> Elyakov Pacific Institute of Bioorganic Chemistry, Far-Eastern Branch of the Russian Academy of Sciences, Pr. 100-letiya Vladivostoka 159, Vladivostok 690022, Russian Federation

<sup>c</sup> Institute for Automation and Control Processes, Far Eastern Branch of the Russian Academy of Sciences, ul. Radio 5, Vladivostok 690041, Russian Federation

<sup>d</sup> Institute of Experimental Medicine, Almazov National Medical Research Centre, Akkuratova ul. 2, St. Petersburg 197341, Russian Federation

<sup>e</sup> Tyumen State University, ul. Volodarskogo 6, Tyumen 625003, Russian Federation

## ARTICLE INFO

## Keywords:

Chitosan

Carrageenan

Polyelectrolyte complex

Pervaporation

## ABSTRACT

A polyelectrolyte complex (PEC) was prepared from chitosan (CS) and  $\lambda$ -carrageenan ( $\lambda$ -CAR) using a layer-by-layer deposition of polyion solutions on a plated nonporous support. This material was then used as a multilayer membrane for the pervaporation separation of aqueous ethanol solutions. The fabricated complex film (25–30  $\mu\text{m}$  thick) was a multilayer system ( $\lambda$ -CAR-PEC-CS) containing a polycation CS (MW  $3.1 \times 10^5$ , DDA 0.93), a polyanion  $\lambda$ -CAR (MW  $3.5 \times 10^5$ , extracted from the alga *Chondrus armatus*), and a PEC layer formed between the two polyion layers. X-ray diffraction indicated a significant structuring of the film in the region of the composite PEC-CS bilayer. The structural and morphological characteristics of the CS surface in the multilayer membrane, as revealed by atomic force microscopy, were close to the characteristics of the dense CS film. However, this structure changed following pervaporation (i.e., the distinct spherical structures on the surface disappeared). Similarly, the initially loose surface of  $\lambda$ -CAR in the composite changed to an ordered domain after pervaporation. The transport properties of the pervaporation membranes were tested by examining the separation of ethanol-water mixtures of different compositions. The flux increased with an increase in the weight percentage of water in the feed mixture, but the separation capacity of the membrane was unchanged. In a range of feed concentrations of 50–94 wt%, the membrane mainly releases water with a corresponding concentration in the permeate of 99.9–99.8 wt% and substantial fluxes of  $0.003\text{--}1.130 \text{ kg m}^{-2} \text{ h}^{-1}$  at  $40^\circ\text{C}$ . The obtained results indicate significant prospects for the use of non-gelling type CARs for the formation of highly effective pervaporation membranes.

## 1. Introduction

Pervaporation has gained wide acceptance as a membrane separation method and is recognized as the most adaptable technique for the separation of water-organic mixtures (Bolto, Hoang, & Xie, 2011; Kujawski, 2000; Ong et al., 2016). As a rule, dehydrating pervaporation membranes are prepared from hydrophilic polymers containing specific functional fragments (e.g., sulfo, carboxyl, amino, or hydroxyl groups) (Namboodiri, Ponangi, & Vane, 2006; Urtiaga et al., 2007; Wang, Li, & Wang, 2001). These fragments take part in the formation of a hydration shell, which then allows the selective mass transfer of water molecules (Figoli, Santoro, Galiano, & Basile, 2015; Korngold, Zisner, & Bejerano, 2016; Uragami, 2017). Several authors have

demonstrated a greater effectiveness of hydrophilic pervaporation for membranes prepared from polyelectrolyte complexes (PEC) than from individual polymers (Rachipudi, Kittur, Choudhari, Varghese, & Kariduraganavar, 2009; Wang et al., 2013). However, the role of PEC in the separation process, and the mechanism of selective transport of polar multiple-charged ions through this type of membrane, remain to be established. Most authors maintain that the unique properties of PEC reflect the existence of a specific hydrophilic-hydrophobic balance that can be easily changed by varying the composition of the complexes and the conditions of their preparation (Krayukhina, Samoilova, & Yamskov, 2008; Zhao, An, Ji, Qian, & Gao, 2011).

A correlation has been observed between the swelling of a membrane and its pervaporation properties for the separation of aliphatic

\* Corresponding author at: Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr. VO 31, St. Petersburg 199004, Russian Federation.  
E-mail address: [yury\\_skorik@mail.ru](mailto:yury_skorik@mail.ru) (Y.A. Skorik).

alcohol/water mixtures. The efficiency of separation of these mixtures is typically estimated using the values of the permeation rate and separation factor. In the majority of cases, an increasing concentration of water in the feed decreases the separation factor and increases the permeation rate because of the increase in the mesh size of the PEC network. When the size of the molecules in the feed does not exceed the mesh size of the swollen polymer network, the permeation rates of water and alcohol show no significant differences. However, the membrane transport properties can depend on the method used for PEC layer formation on a porous substrate surface. Nevertheless, deposition from a solution of polyelectrolytes or layer-by-layer deposition both create effective membranes for hydrophilic pervaporation (Kuznetsov et al., 2003).

The separation characteristics of multilayer PEC membranes formed by combining layers of polymeric electrolytes depend largely on the strength of the interactions between the macrocounterions. This interaction can change the structure of the film towards increasing order. This factor of interpolymer interaction is believed to prevail over other “structural” factors, such as the degree of crosslinking, the flexibility of the backbone, the presence of aromatic fragments, etc. Thus, obtaining regular non-defect layers of interpolymer complexes with good separating capability is considered possible only when using polyelectrolytes that have a high charge density (Decher & Schlenoff, 2003; Toutianoush & Tieke, 2002).

The interaction between polyanions and the chitosan (CS) in various complexation processes has received considerable research attention. CS is a partially or completely deacetylated derivative of chitin and can form non-covalent complexes with polyanions, suggesting the possibility of numerous practical applications (Krayukhina, Samoilova, & Yamskov, 2008; Shieh & Huang, 1997; Zhao et al., 2009). The formation of membrane diffusion layers from CS-based PECs can create high-performance pervaporation membranes for the isolation of polar liquids (and water, in the first instance) from organic or water-organic mixtures (Ageev, Kotova, Skorikova, & Zezin, 1996; Ageev et al., 1998; Knop, Thielking, & Kulicke, 2000; Kulicke & Nottelmann, 1987; Kuznetsov et al., 2003; Skorikova et al., 1996). Shieh & Huang (1997) used a CS-polyacrylic acid complex membrane for dehydration of 95 wt% aqueous ethanol at 30 °C by pervaporation, and obtained a flux of 33 g m<sup>-2</sup> h<sup>-1</sup> with a separation factor of 2216. The studies in this field have shown that the transport properties of CS-containing membranes are influenced by a number of factors, including the chemical structure of the polymers, their location, the numbers of charged groups, the composition of the complexes, the method of membrane preparation, and subsequent treatments. Formation of a PEC membrane is accompanied by a weak cross-linking of the macromolecules in the sites where the counterions are in contact. The addition of polymers with an oppositely charged backbone or side groups leads to electrostatic interactions of the charged polymers and the formation of a supramolecular aggregated structure that can stabilize the membrane. The polymeric character of the counterions results in a strong dependence of the membrane properties on the molar mass and on the charge distribution along the chitosan chain (Wang, Li, Lu, & Wang, 1997). Most often, synthetic polyanions are used to realize interpolymer contacts with CS during formation of defect-free composite PEC layers (Choudhari, Premakshi, & Kariduraganavar, 2016; Rachipudi, Kittur, Choudhari, Varghese, & Kariduraganavar, 2009; Shieh & Huang, 1997; Wang et al., 2013). The preparation of these structures from natural polysaccharides or their derivatives was rarely attempted due to difficulties in the techniques (Zhao et al., 2009).

Anionic polysaccharides, which are remarkable for the diversity of their structures, are attractive as polymeric counterions for use in the formation of PECs with CS. Cellulose derivatives, alginate or hyaluronate, dextran sulfate, and other polysaccharides have been used as macrocounterions during the preparation of multilayer membranes of different types (Krasemann & Tieke, 2000). A correlation was shown between the swelling of the CS-sulfoethylcellulose simplex membranes

and their molecular parameters (Clasen, Wilhelms, & Kulicke, 2006). Huang et al. (2000) prepared CS-alginate membranes in both free-standing and composite forms for use in pervaporation of aqueous ethanol or isopropanol. Kim, Lee, & Lee (2007) reported the permselectivity of CS-alginate membranes for aqueous alcohol solutions. Zhao et al. (2009) reported a flux of 1.14 kg m<sup>-2</sup> h<sup>-1</sup> with a permselectivity of 1062 through a CS-carboxymethylcellulose membrane.

Our previous work demonstrated that application of solutions of hyaluronic and alginic acids, sulfoethylcellulose, or κ/β-carrageenan (κ/β-CAR) onto a CS gel film resulted in the formation of a PEC layer at the interface. The establishment of this complex is accompanied by an ordering of the CS chains in the near-surface layer; thus, the microstructure of the complex depends on the nature of the interacting polymers. A rational choice for the polyelectrolyte pair, together with the development of new analytical techniques for the study of multilayer polymer composites, could therefore reveal radically new information regarding the role of PEC in membrane formation and provide insight into the membrane structure and the notion of “transport channels” (Baklagina et al., 2013; Petrova et al., 2016).

The presence of negatively charged sulfate groups in CAR allows this polysaccharide to form a PEC with CS (Hamman, 2010; Volod'ko et al., 2014). CARs are complex families of water-soluble, linear, sulfated galactans, whose basic structural units are disaccharides consisting of alternating β-1,4- and α-1,3-linked D-galactose residues. The structural diversity of CARs arises due to the presence 3,6-anhydrogalactose, the location and number of various sulfate groups, and the irregular polymer chain (Yermak & Khotimchenko, 2003).

Previous studies on a pervaporation membrane with a separating layer containing PEC based on κ-CAR and poly{1,3-bis[4-butylpyridinium]propane bromide} (Jegal & Lee, 1996) established the efficiency of this membrane for the dehydration of a 90 wt% aqueous ethanol solution. Interestingly, the polyion complex membranes made from amorphous κ-CAR and highly crystalline poly{1,3-bis[4-butylpyridinium]propane bromide} were entirely amorphous. These polyion complex membranes showed very high permselectivity and very high permeability for the pervaporation separation of a water-ethanol mixture over a wide temperature range. The reasons for this effect can be attributed to the excellent hydrophilicity of the polyion complex surface layers and the high glass transition temperature of κ-CAR. The higher ion content in the polyion complex layers of the membranes provided a higher permselectivity and higher permeability. The polyion complex membrane showed a separation factor of about 12,000 and a flux of 600 g m<sup>-2</sup> h<sup>-1</sup> for a water-ethanol mixture (90 wt % EtOH) at 60 °C. The separation properties of this polyion complex membrane were quite comparable to those of known high-performance composite membranes.

For these reasons, the study of multilayer films based on CAR and CS is worthwhile. CAR molecules may acquire various conformations in solutions. The molecules of gel-forming CARs contain 3,6-anhydrogalactose fragments, which impart rigidity to the polymer chain and allow a spiral conformation; by contrast, non-gel-forming CARs contain large numbers of anionic groups and form random coils (Yermak & Khotimchenko, 2003). λ-CAR is one of the non-gel-forming types, so its structure may play a critical role in the formation of PEC with CS in a multilayer film.

The aim of the present work was to prepare multilayer composite membranes as self-standing non-porous films based on λ-CAR and CS polysaccharide counterions. These films were then evaluated in connection with their structure and morphological features for their performance as dehydrating pervaporation membranes for the separation of water-alcohol mixtures.

Download English Version:

<https://daneshyari.com/en/article/7784417>

Download Persian Version:

<https://daneshyari.com/article/7784417>

[Daneshyari.com](https://daneshyari.com)