Some Physicochemical Measurements of Chitosan Polymer in Acetic Acid–Water Mixtures at Different Temperatures

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INTRODUCTION
Chitin, a naturally occurring polymer, is the second most abundant organic resource on the earth next to cellulose. It is an exoskeleton of crustaceans, cuticle of insects, and cell wall of fungi. Because of its biodegradability, it is frequently used as a membrane material to develop drug-loaded controlled-release formulations as well as a membrane in the pervaporation separation of water-acetic acid mixtures. Deacetylation of chitin yields chitosan, which is relatively reactive. It is important to know its physicochemical properties at lower concentrations of acetic acid in aqueous media because the degree of acetylation of chitosan varies depending on the number of acetyl groups present. This need prompted us to measure density, \( \rho \), viscosity, \( \eta \), refractive index for the sodium D line, \( n_D \), and speed of sound, \( v \), in 0.05 to 0.20 mass % of chitosan in acetic acid–water mixtures ranging in mole fraction from 1.6 to 9.4 \( \times 10^{-3} \). At higher amounts of acetic acid, chitosan is insoluble, making the measurements difficult. Therefore, the properties have been measured in aqueous acetic acid mixtures at lower concentration of acetic acid. To the best of our knowledge, no such data on chitosan are available in the literature.

EXPERIMENTAL
Materials and methods
Medium molecular weight chitosan [product batch 9012-76-4] with 75–85 % deacetylated chitosan was purchased from Aldrich, Milwaukee, WI. Acetic acid [product batch 58-0994-494-138931] was purchased from s.d. fine Chemicals Ltd., Mumbai, India. The acetic acid purity, as assayed by gas chromatography, was 99.7 mol %, and its density was 1.0490 g/cm\(^3\) at 293.15 K. Double-distilled deionized water was used throughout the research.

Acetic acid–water mixtures were prepared by mass within an uncertainty of ±0.01 mg using an electronic single pan Mettler balance (AE 240, Switzerland). Four chitosan concentrations, expressed in 0.05, 0.10, 0.15, and 0.20 mass % units, were prepared in different compositions of acetic acid–water mixtures. The reproducibility in mole fraction of acetic acid–water mixtures was within ±0.0002 units.

Solution densities were measured within an uncertainty of ±0.0005 g • cm\(^{-3}\) with a pycnometer having a bulb volume of 10 cm\(^3\) and a capillary bore with an internal diameter of 1 mm. Speeds of sound values were measured within an uncertainty of ±2 m • s\(^{-1}\) with a variable path single crystal interferometer (Mittal Enterprises, Model M-84, New Delhi). The data were collected at a frequency of 1 MHz, and the instrument was calibrated with water and benzene. Refractive indices for the sodium D-line were measured to an uncertainty of ±0.0001 units with a thermostatically controlled Abbe Refractometer (Atago 3T, made in Japan). The calibration procedure of the refractometer is the same as given earlier.

The molecular mass of chitosan was calculated by measuring the viscosity (uncertainty, ±0.001 mPa • s) of 0.05, 0.10, 0.15, and 0.20 mass % solutions of chitosan in 2% aqueous acetic acid at 303.15 K with the Scott Gerate viscometer (AVS 320, Germany) as per the detailed procedure published earlier. The intrinsic viscosity \( [\eta] \) was calculated from the reduced viscosity versus concentration plot shown in Figure 1. Then, by using the Mark–Houwink–Sakurada equation, the molecular mass of chitosan was calculated.

Figure 1 Reduced viscosity versus concentration of chitosan in acetic acid at 303.15 K.
Synthesis and Characterization of Polyacrylamide-Grafted Sodium Alginate Copolymeric Membranes and Their Use in Pervaporation Separation of Water and Tetrahydrofuran Mixtures

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Abstract: Polyacrylamide-grafted sodium alginate (PAAm-g-Na-Alg) copolymeric membranes have been prepared, characterized, and used in the pervaporation separation of 10–80 mass % water-containing tetrahydrofuran mixtures. Totally three membranes were prepared: (1) neat Na-Alg with 10 mass % of polyethylene glycol (PEG) and 5 mass % of polyvinyl alcohol (PVA), (2) 46 % grafted PAAm-g-Na-Alg membrane containing 10 mass % of PEG and 5 mass % of PVA, and (3) 93 % grafted PAAm-g-Na-Alg membrane containing 10 mass % of PEG and 5 mass % of PVA. Using the transport data, important parameters like permeation flux, selectivity, pervaporation separation index, swelling index, and diffusion coefficient have been calculated at 30°C. Diffusion coefficients were also calculated from sorption gravimetric data of water-tetrahydrofuran mixtures using Fick's equation. Arrhenius activation parameters for the transport processes were calculated for 10 mass % of water in the feed mixture using flux and diffusion data obtained at 30, 35, and 40°C. The separation selectivity of the membranes ranged between 216 and 591. The highest permeation flux of 0.677 kg/m² h was observed for 93 % grafted membrane at 80 mass % of water in the feed mixture.

Key words: pervaporation; tetrahydrofuran; sodium alginate; polyacrylamide; polyethylene glycol

Introduction

Pervaporation (PV) is a membrane-based separation technique used extensively in the separation of aqueous-organic mixtures.1-4 The method is relatively inexpensive and eco-friendly, yet its commercial exploitation has not yet been achieved satisfactorily. In earlier studies,5,6 several hydrophilic membranes (e.g., polyvinyl alcohol) have been used in separating the aqueous-organic mixtures. However, the use of a natural polymer like sodium alginate (Na-Alg) along with a synthetic polymer like polyacrylamide (PAAm) may be advantageous, particularly to increase the flux.6-10 In our earlier study,6 we found that when Na-Alg was blended with polyvinyl alcohol (PVA), flux of the blend membrane was increased with increasing amount of PVA. In continuation of this study and as a part of our ongoing research program on membrane-based processes, we present here the synthesis of grafted copolymeric membranes of PAAm and Na-Alg for PV separation of water and tetrahydrofuran (THF) mixtures. Water and THF form azetropes at 6.7 mass % of water,11 and hence it is difficult to separate the components by the so-called conventional techniques like distillation, etc. Even though some reports have already been published in the literature on the PV separation of water and THF mixtures,12-17 the present paper reports on the improved selectivity to water by the use of new membranes developed.

Experimental

Materials

Sodium alginate (LR) and poly(vinyl alcohol) (molecular weight, 125,000), glutaraldehyde (25 mass % aqueous solution) (LR), and acetone were obtained from S. D. Fine Chem. Ltd., Mumbai, India. The A. R. grade tetrahydrofuran (anhydrous) was supplied by Spectrochem Pvt. Ltd., Mumbai, India. Polyethylene glycol (PEG-200) and potassium persulfate were respectively procured from Merck and Sisco-Chem Industries, Mumbai, India. All these chemicals were used as such and solutions were prepared from double distilled water.

Preparation of grafted copolymers

About 10 g of Na-Alg was dissolved in 100 mL of distilled water at 60°C with constant stirring under nitrogen atmosphere in a three-necked round-bottom flask.
Syntheses and Characterization of Blend Membranes of Sodium Alginate and Poly(vinyl alcohol) for the Pervaporation Separation of Water + Isopropanol Mixtures

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ABSTRACT: The blend membranes of sodium alginate and poly(vinyl alcohol) have been prepared by physical mixing in different ratios (75, 50, and 25%) of sodium alginate with poly(vinyl alcohol). The membranes were crosslinked with glutaraldehyde and used in the pervaporation separation of water + isopropanol mixtures at 30°C. The crosslinking reaction was confirmed by Fourier transform infrared spectra. Permeation flux increased with an increase in mass % of water in the feed mixture as well as with an increase in the amount of poly(vinyl alcohol) in the blend, but separation selectivity decreased. Diffusion coefficients of water + isopropanol mixtures have been calculated using the Pick's equation from the sorption data. Arrhenius activation parameters were calculated for 10 mass % of water in the feed mixture using the values of flux and diffusion coefficients obtained at 30, 40, and 50°C. The diffusion and pervaporation results have been explained on the basis of solution-diffusion principles.

INTRODUCTION

Pervaporation (PV) separation based on polymeric membranes has been widely used in separating alcohols from their aqueous mixtures. A good pervaporation membrane should exhibit high permeation flux and high separation selectivity. The simultaneous enhancement of both these parameters has been a challenge in PV separation industries. For aqueous mixtures, hydrophilic polymers have good separation characteristics due to their strong affinity towards water, but the main drawback of such polymers is their excessive swelling due to hydrogen bonding between hydrophilic functional groups of the polymer and the water molecule. Introduction of hydrophilic groups on the membrane results in high swelling and low water selectivity. To suppress this effect three-dimensional crosslinked network polymers have been proposed. Among the hydrophilic polysaccharide polymers, sodium alginate has gained widespread application as a membrane material because it exhibits high separation selectivity and flux when compared to many other hydrophilic polymers.

In the present study, blend membranes of sodium alginate (Na-Alg) and poly(vinyl alcohol) (PVA) are prepared and used for the PV separation of isopropanol (Iso-OH) and water mixtures. There have been very few limited studies in the previous literature on the PV separation of blend membranes derived from Na-Alg and PVA. For instance, Moon et al. have prepared the sodium alginate and chitosan two-ply membranes and used in the PV dehydration of Iso-OH. Recently, the Na-Alg membranes have been studied for the PV separation of aqueous-organic mixtures. In continuation of our ongoing program of research in developing newer membranes, we now extend our study on the pervaporation separation of water + Iso-OH mixtures using the blend membranes of Na-Alg and PVA. It is hoped that the use of a more flexible PVA will enhance the overall membrane flexibility of the otherwise rigid Na-Alg membrane. This would make the blend membrane more suitable for the PV separation of polar molecules such as water from water + isopropanol mixture. The important PV separation parameters, viz., sorption, diffusion, sorption selectivity, pervaporation separation index, enrichment factor, and flux have been studied. Activation parameters for the solvent flux and diffusion have been computed from the Arrhenius relationship. The results are discussed in terms of the diffusion anomalies.

EXPERIMENTAL

Materials

Sodium alginate (LR grade) and poly(vinyl alcohol), M.W. 125,000, isopropanol (AR grade), glutaralde-